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[Contributions from the Sheffield Laboratory of Yale University.]

CLXVIII.—RESEARCHES ON PYRIMIDINES: THE PREPARATION OF 1,4-DIMETHYLURACIL AND OF THE MONOBENZYL DERIVATIVES OF 4-METHYLURACIL.[1]

[FORTY-FOURTH PAPER.]

BY HENRY L. WHEELER AND DAVID F. MCFARLAND.

Behrend[2] has shown, in his work on the methylation of 4-methyluracil with alkali and methyl iodide, that the three products 1,4-dimethyluracil, 3,4-dimethyluracil, and 1,3,4-trimethyluracil, are all formed and have to be dealt with in addition to unaltered material.

List[3] found that 2-thio-4-methyluracil (I.) is readily methylated and that the alkyl group unites with the sulphur, producing 2-methylmercapto-4-methyl-6-oxypyrimidine (II.). List did not determine what was formed on further alkylation.

[1] Part of a Thesis presented by David F. McFarland for the Degree of Ph.D., Yale, 1909.

[2] Behrend and Dietrich: Ann. Chem. (Liebig), **309**, 265 (1899). Behrend and Meyer: Ber. d. chem. Ges., **33**, 624 (1900). Behrend and Thurn: Ann. Chem. (Liebig), **323**, 160 (1902).

[3] Ann. Chem. (Liebig), **236**, 12 (1886).

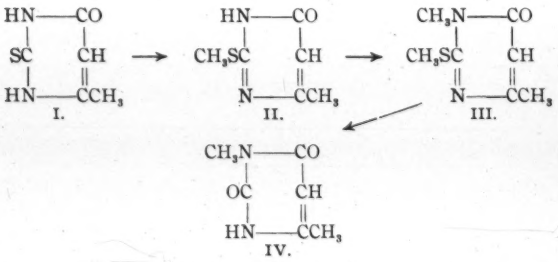
In previous papers from this laboratory it has been shown that 2-mercapto-6-oxypyrimidines usually give a mixture of the 1- and 3-alkyl derivatives on further alkylation.[1]

We will now show that the potassium salt of List's 2-methylmercapto-4-methyl-6-oxypyrimidine, in alcoholic solution, alkylates almost entirely in the 1-position with methyl iodide and that 1,4-dimethyl-2-methylmercapto-6-oxypyrimidine (III.) is formed. There are indications also, in this reaction, of the formation of 2-methylmercapto-4-methyl-6-methoxypyrimidine in small amount.

Since the alkylmercaptopyrimidines easily evolve mercaptan and form the corresponding uracil derivatives on boiling with hydrochloric acid, this method is the best (*Darstellung*) for the preparation of 1,4-dimethyluracil (IV.).

By condensing acetoacetic ethyl ester with thiourea in alcoholic solution and in the presence of two molecular proportions of sodium ethylate, a quantitative yield of List's 2-thio-4-methyluracil (I.) may be obtained. The condensation also takes place in alkaline aqueous solution but the yield is not as good. Even this process is far superior to the original methods.[2]

The steps in the synthesis of 1,4-dimethyluracil may be represented as follows:



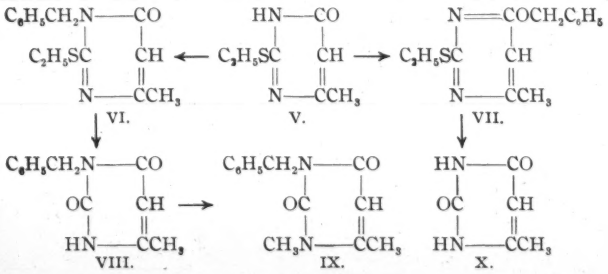
Acetoacetic ethyl ester condenses with ethylpseudothiourea,

[1] For a list of these cases see our forty-third paper on pyrimidines, THIS JOURNAL, **42**, (1909).

[2] Nencki and Sieber: J. prakt. Chem., [2] **25**, 72 (1882). List: *Loc. cit.*

$H_2N-C(SC_2H_5)NH$, in alkaline aqueous solution more smoothly and gives a larger yield (over 80 per cent) of mercaptopyrimidine than in the case of the corresponding condensations of the sodium salts of either ethyl formylacetate or ethyl formylpropionate.

When 2-ethylmercapto-4-methyl-6-oxypyrimidine (V.), prepared in this manner, was treated with sodium hydroxide and benzyl chloride, a mixture of 1-benzyl-2-ethylmercapto-4-methyl-6-oxypyrimidine (VI.) and 2-ethylmercapto-4-methyl-6-benzyloxypyrimidine (VII.) was obtained. This mixture, which was obtained as an oil insoluble in alkali, could not be separated by distillation under reduced pressure. When it was boiled with hydrochloric acid mercaptan escaped and a new benzyl-4-methyluracil, melting at 194°, along with 4-methyluracil, was obtained.

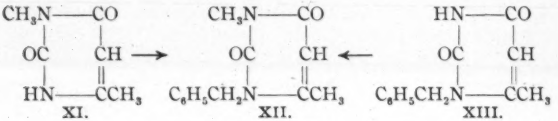


Hagen[1] described a benzyl-4-methyluracil melting at 233° which he obtained in very small amount—the quantity being only sufficient for analysis—by heating the dry potassium salt of 4-methyluracil at a high temperature with benzyl chloride. This substance is given in Beilstein's *Handbuch*[2] as 1-benzyl-4-methyluracil (VIII.).

We now find that this is incorrect and that the compound is 3-benzyl-4-methyluracil (XIII.). The proof of the structure of these compounds was obtained as follows: 1,4-Dimethyl-

[1] Ann. Chem. (Liebig), **244**, 9 (1888).
[2] [3] **2**, 529.

uracil (XI.) was treated with potassium hydroxide and benzyl chloride in alcoholic solution. This gave 1,4-dimethyl-3-benzyluracil (XII.), melting at 85°–86°. Hagen's benzylmethyluracil, which we find is easily obtained, along with the isomer melting at 194°, when 4-methyluracil, potassium hydroxide and benzyl chloride are warmed in alcoholic solution, was then methylated; the same dimethylbenzyluracil melting at 85°–86° was thereby obtained.

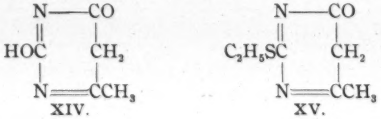


XI. XII. XIII.

When the new 1-benzyl-4-methyluracil (VIII.) was methylated it gave the isomeric 1-benzyl-3,4-dimethyluracil (IX.), melting at 164°.

The possibility of an alkylation taking place in the 5-position in the case of pyrimidines derived from acetoacetic ester had to be considered, at this point, before the above results could be taken as proof of the structures assigned to the benzyl compounds in question. Barbituric acid or 2,4,6-trioxypyrimidine alkylates under the same conditions in the 5-position.[1]

From the analogy which exists between acetoacetic ester and malonic ester it might be expected that 4-methyluracil or 2-ethylmercapto-4-methyl-6-oxypyrimidine might react in the tautomeric forms represented by formulas (XIV.) and (XV.) and yield 5-benzyl derivatives.

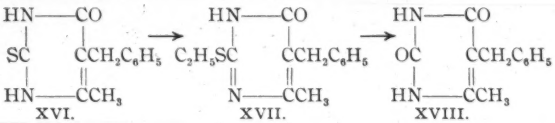


XIV. XV.

In order to prepare 4-methyl-5-benzyluracil (XVIII.) it was necessary to condense benzylacetoacetic ester with a urea

[1] Conrad and Gutzeit: Ber. d. chem. Ges., **14**, 1643 (1881); **15**, 2846 (1882). Fischer and Dilthey: Ann. Chem. (Liebig), **335**, 338 (1904).

derivative. This ester proved to be one of those β-ketone esters which failed to condense satisfactorily by the general method with the pseudothioureas in aqueous solution. We find, however, that it condenses in alcoholic solution with thiourea in the presence of sodium ethylate, giving the sodium salt of 2-thio-4-methyl-5-benzyluracil (XVI.). In order to desulphurize this it was found best to convert it into 2-ethyl mercapto-4-methyl-5-benzyl-6-oxypyrimidine (XVII.) which, on boiling with hydrochloric acid, easily gave the desired 4-methyl-5-benzyluracil (XVIII.) melting at 249°–250°.

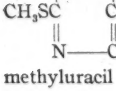


XVI. XVII. XVIII.

Since this compound, melting at 249°–250°, is different from either of the above benzylmethyluracils it follows that in the alkylation of the pyrimidines derived from acetoacetic ester, under the conditions stated, the benzyl group does not enter the 5-position, and that the various benzyl compounds are correctly represented by the formulas given above. The isomeric benzyloxypyrimidines would not be stable when boiled with hydrochloric acid and are therefore excluded. This otherwise completes the list and settles the structure of the monobenzyl derivatives of 4-methyluracil.

EXPERIMENTAL PART.

1,4-Dimethyl-2-methylmercapto-6-oxypyrimidine,



—An almost quantitative yield of 2-thio-4-methyluracil was usually obtained when 30 grams of acetoacetic ester and two molecular quantities of sodium ethylate, made by dissolving 10.6 grams of sodium in 200 cc. of absolute alcohol, were warmed for half an hour with 17.5 grams of thio-

urea. On evaporating the alcohol on the steam bath, which appears to render the condensation more nearly complete, the sodium salt of 2-thio-4-methyluracil remained. This salt easily dissolved in water. On addition of acetic acid to the solution, 2-thio-4-methyluracil was precipitated. The precipitate is apt to carry down with it some of the sodium salt, and it was found advisable to warm it, after filtering, with water acidified with acetic acid. Then on washing with water it is obtained pure and free from sodium.

When 2-thio-4-methyluracil is treated with two molecular proportions of potassium hydroxide and methyl iodide a considerable quantity of 2-methylmercapto-4-methyl-6-oxypyrimidine is obtained. In order to produce a satisfactory alkylation on the nitrogen it is necessary to use a greater excess of alkali and methyl iodide. Potassium hydroxide gives better results in nitrogen alkylation than sodium hydroxide.

Thirty grams of 2-thio-4-methyl-6-oxypyrimidine were dissolved with 35 grams of potassium hydroxide in 150 cc. of absolute alcohol. The potassium salt formed was much more soluble than the free pyrimidine. After cooling the solution, 94 grams of methyl iodide, an excess of 4 grams over that calculated for 3 molecular quantities, were gradually added and the mixture was allowed to stand two days. At the end of that time, about 6 hours' gentle heating on the steam bath was required to complete the reaction so that the solution gave no alkaline test with moist turmeric paper. The alcohol was then evaporated, under diminished pressure, and the solid residue was treated with dilute sodium hydroxide. The undissolved portion was filtered and washed with a little water. Twenty-five and one-tenth grams of 1,4-dimethyl-2-methylmercapto-6-oxypyrimidine melting at 85°–90° were obtained. An additional 2.3 grams were recovered by shaking the alkaline mother liquor with ether, making the total yield of the compound 27.4 grams, or 76.4 per cent. of the calculated yield. From the alkaline solution 4.5 grams of 2-methylmercapto-4-methyl-6-oxypyrimidine, formed by incomplete methylation, were obtained on acidifying. Al-

lowing for this, the yield of 1,4-dimethyl-2-methylmercapto-6-oxypyrimidine becomes 91.2 per cent of the calculated.

In another experiment where only two molecular proportions of alkali and of methyl iodide were used with 27 grams of 2-thio-4-methyluracil, the amount of intermediate 2-methylmercapto-4-methyl-6-oxypyrimidine was largely increased, 8 grams of it being formed, with a corresponding decrease of dimethylmercapto compound. This shows that a large excess of alkali and of methyl iodide is necessary in order to completely methylate 2-thiouracil.

A small quantity of oily substance, with a pungent odor resembling that of parsnips, coated the material insoluble in alkali. It is probable that this oil is a 6-methoxy derivative but not enough was obtained to permit of its identification. When the material insoluble in alkali was crystallized from water it gave needles which melted sharply at 94° and the results on analysis agreed with those calculated for 1,4-dimethyl-2-methylmercapto-6-oxypyrimidine.

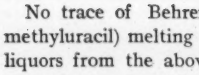
	Calculated for $C_7H_{10}ON_2S$.	Found.
N	16.22	16.47

The substance is readily soluble in alcohol and boiling water, crystallizing from aqueous solutions in silky needles. It is extremely soluble in ether, chloroform and benzene, and rather difficultly soluble in petroleum ether. It sublimes readily at the temperature of the steam bath, condensing again in fine silky needles. It is easily volatile with steam, and solutions containing it cannot be evaporated on the steam bath without loss.

Action of Hydrochloric Acid: 1,4-Dimethyluracil.—The above 1,4-dimethyl-2-methylmercaptopyrimidine was boiled for one hour with strong hydrochloric acid under a reflux condenser to prevent loss of the volatile compound. By this treatment it was quantitatively converted into Behrend's β-dimethyluracil (1,4-dimethyluracil). One recrystallization from hot water gave material melting sharply to a clear oil at 260°–261°.

No trace of Behrend's isomeric α-dimethyluracil (3,4-dimethyluracil) melting at 220° was found in any of the mother liquors from the above. It is reasonably certain, therefore, that the corresponding 2-methylmercapto-3,4-dimethyl-6-oxypyrimidine was not formed in appreciable quantities.

1-Benzyl-2-ethylmercapto-4-methyl-6-oxypyrimidine,



2-Ethylmercapto-4-methyl-6-oxypyrimidine was prepared by condensing acetoacetic ethyl ester with ethyl pseudothiourea in aqueous, alkaline solution; from 54.5 grams of acetoacetic ester a yield of 58.5 grams of crude mercapto compound was obtained, or 81.5 per cent of the calculated.

Twenty grams of this compound were added to a solution of 2.95 grams of sodium in 60 cc. of alcohol. After complete solution had been effected 16.2 grams of benzyl chloride were added and the mixture was heated on the water bath until no further alkaline reaction could be obtained with moist turmeric paper. This required about four hours. The alcohol was then evaporated under diminished pressure and the residue treated with 20 cc. of water and 10 cc. of dilute sodium hydroxide. A heavy oil remained undissolved. This was shaken out with ether; the ether solution was washed with water to remove alcohol, dried over solid potassium hydroxide, and filtered into a weighed flask. After evaporating the ether, 20.7 grams of oil remained, or 68 per cent of the calculated monobenzyl derivative. From the above alkaline solution 9 grams of unaltered substances and from the oil 6 grams of low-boiling material were obtained. Allowing for these weights, the yield of monobenzyl derivative is 87.5 per cent.

The oil was distilled at 22 mm. pressure and after about six grams of low-boiling oil (benzyl chloride?) had distilled over, the temperature rose to 224° and a little over 10 grams of material distilled between this and 236°. The greater part boiled near 227°. The temperature rose slowly, toward

the last to 260°, where the distillation was stopped. The fractions obtained were only slightly colored. None of them gave any solid even when cooled to —15°. Analyses were made of two separate fractions, one (A) boiling at 227°–228°, and the other (B) at 228°–260°. Both gave excellent results for a monobenzyl derivative of 2-ethylmercapto-4-methyl-6-oxypyrimidine.

	Calculated for $C_{14}H_{16}ON_2S$.	Found. A.	B.
N	10.77	10.63	10.62

Action of Hydrochloric Acid: 1-Benzyl-4-methyluracil.—Two grams of the above fraction B were boiled for two hours with 15 cc. of concentrated hydrochloric acid, during which time mercaptan was evolved. The solution was evaporated to dryness, a solid residue weighing 1.3 grams, which nearly all dissolved in boiling water remaining. After filtering off the small amount of gummy residue which did not dissolve, a crystalline mass separated on cooling. It dissolved in boiling alcohol, and, on cooling gave colorless, rounded, lozenge-shaped crystals melting to a clear oil at 194°. Analysis showed this to be a monobenzyl-4-methyluracil.

	Calculated for $C_{13}H_{12}O_2N_2$.	Found.
N	12.96	12.93

The compound dissolves easily in cold chloroform, moderately in hot alcohol, and rather difficultly in hot water. The crystals from alcohol are characteristic.

By evaporation of the aqueous mother liquor from the above compound, material was obtained which crystallized in clusters of fine needles. It had no sharp melting point but decomposed at 270°–300°. Analyses of this material gave results which agreed with those calculated for 4-methyluracil. When it was mixed with pure 4-methyluracil, the decomposition point was not lowered. From the two grams of oil hydrolyzed there were obtained about 0.3 gram of 1-benzyl-4-methyluracil and 0.6 gram of 4-methyluracil. This result indicates that the fraction of oil boiling at 228°–260° consisted about

one-third of 1-benzyl-2-ethylmercapto-4-methyl-6-oxypyrimidine and two-thirds of the isomeric 2-ethylmercapto-4-methyl-6-benzyloxypyrimidine.

A similar hydrolysis of fraction A of the oil yielded approximately equal proportions of 4-methyluracil and 1-benzyl-4-methyluracil, so that this fraction consisted of a corresponding mixture of the mercaptobenzyl compounds. Repeated fractional crystallization of all the residues from this experiment failed to give any other substance besides the two described. No trace of the monobenzyl-4-methyluracil described by Hagen[1] was found, although a painstaking search was made for it.

Action of Benzyl Chloride upon 4-Methyluracil: 3-Benzyl-4-methyluracil.—The 4-methyluracil for this experiment was made by boiling 2-ethylmercapto-4-methyl-6-oxypyrimidine with strong hydrochloric acid until mercaptan ceased to be evolved. It was purified by crystallization from water.

Five and a half grams of 4-methyluracil were heated with 2.44 grams of potassium hydroxide in 50 cc. of absolute alcohol. Complete solution did not take place until a further addition of 50 cc. of alcohol and 28 cc. of water had been made. Six grams of benzyl chloride, or one-half gram excess over the calculated, was then added and the mixture heated for three hours on the steam bath or until no alkaline reaction was obtained.

On evaporating the alcohol, a partially solidified mass remained. Part of this dissolved when warmed with dilute sodium hydroxide. The insoluble part formed a resinous semisolid on cooling; this gum could not be induced to crystallize.

From the alkaline solution acetic acid precipitated a mixture. This was boiled with about 50 cc. of alcohol. The portion which did not dissolve proved to be chiefly 4-methyluracil. On cooling the alcoholic solution, pearly, irridescent, diamond-shaped plates separated which melted about 220°–235°, at least 30° higher than 1-benzyl-4-methyluracil. Three crystallizations from alcohol raised the melting point to 233°–

[1] *Loc. cit.*

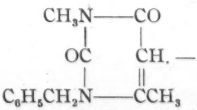
235°. It therefore agreed with that given by Hagen for his benzyl-4-methyluracil. The compound is very difficultly soluble in hot alcohol and still more difficultly in boiling water. It is almost insoluble in cold chloroform. An analysis of the substance melting at 233°–235° gave results agreeing with those calculated for monobenzyl-4-methyluracil.

	Calculated for $C_{12}H_{12}O_2N_2$.	Found.
N	12.96	13.18

The alcoholic mother liquors from this were evaporated to dryness. The remaining material was then shaken with chloroform. The insoluble part proved to be almost pure 3-benzyl-4-methyluracil (Hagen's compound). The chloroform solution was evaporated to dryness and the residue was crystallized from alcohol, whereupon the isomeric 1-benzyl-4-methyluracil was obtained.

A second benzylation of 4-methyluracil, with 7 grams of the pyrimidine and two molecular proportions of potassium hydroxide (6.22 grams) and of benzyl chloride (14.5 grams) in 115 cc. of alcohol and 35 cc. of water, gave 3.6 grams of gum, insoluble in alkali, 2 grams of unaltered 4-methyluracil, and about 2 grams each of the isomeric nitrogen benzyl-4-methyluracils.

1,4-Dimethyl-3-benzyluracil,



— Hagen's benzyl-4-methyluracil melting at 233° (1.6 grams) was dissolved in 90 cc. of methyl alcohol with three molecular proportions of potassium hydroxide and warmed for three hours and a half with methyl iodide (3.25 grams). The alcohol was then evaporated and the residue was stirred with dilute sodium hydroxide. This left 1.8 grams of oil which on cooling solidified. It was dissolved in ether and the clear, filtered solution was allowed to evaporate slowly in a tall test tube. Beautiful, clear, transparent, prismatic tables were then obtained which melted sharply at 85°–86°. When these

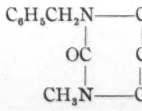
were mixed with 1,4-dimethyl-3-benzyluracil prepared by benzylating 1,4-dimethyluracil the melting point was not lowered. The two preparations agreed in all respects and are identical.

The preparation of this compound from 1,4-dimethyluracil was as follows: Two and eighty-five hundredths grams of 1,4-dimethyluracil and one molecular quantity of potassium hydroxide were dissolved in 120 cc. of 95 per cent alcohol. One molecular portion of benzyl chloride was added and the mixture was heated on the steam bath until a neutral reaction was obtained. A considerable amount of potassium chloride which separated was filtered off and the alcohol was evaporated, a partially solid mass remaining. A portion of this dissolved when treated with sodium hydroxide, leaving 2.1 grams of oil, which finally solidified. When crystallized from ether as described above it melted sharply at 85°–86° and the analytical results were as follows:

	Calculated for $C_{13}H_{14}O_2N_2$.	Found. I.	Found. II.
N	12.17	12.41	12.22

This substance was found to be extremely soluble in alcohol and benzene, much less so in ether, and only slightly in petroleum ether.

1-Benzyl-3,4-dimethyluracil,



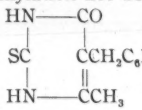
This compound, isomeric with the above, was produced when 1.45 grams of 1-benzyl-4-methyluracil melting at 194° was warmed for about four hours with molecular proportions of potassium hydroxide and methyl iodide in 50 cc. of 95 per cent alcohol. The potassium iodide which separated during the reaction was filtered off and the alcohol evaporated to dryness. The residue was treated with dilute sodium hydroxide, washed with water, and dried. It weighed 1.2 grams, or 76 per cent of the calculated. When crystallized from alcohol, beautiful,

long, colorless prisms melting at 164° to a clear oil, were obtained.

An analysis gave results agreeing with the calculated for 1-benzyl-3,4-dimethyl uracil.

	Calculated for $C_{13}H_{14}O_2N_2$.	Found. I.	II.
N	12.17	12.43	12.32

The alkaline solution above gave 1,4-dimethyluracil when acidified with acetic acid, the alkylation not being complete.

2-Thio-4-methyl-5-benzyluracil,  — Benzyl-

acetoacetic ethyl ester was prepared by the action of benzyl chloride upon the sodium salt of acetoacetic ester, according to the method of Ehrlich.[1] The portion boiling at 194°–204° at 40 mm. pressure was used in the following work, part of which was done by Mr. McKay S. Howard:

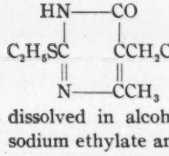
Ten grams of benzylacetoacetic ester and 4 grams of thiourea were added to a solution of sodium ethylate made by dissolving three grams of sodium in 75 cc. of absolute alcohol. The mixture was heated on the steam bath for four hours. The alcohol was then evaporated and the residue was dissolved in water. On the addition of dilute acetic acid 2-thio-4-methyl-5-benzyl-6-oxypyrimidine was precipitated. The yield was 7.4 grams, or 70 per cent of the calculated. The substance was very difficultly soluble in water but more easily in alcohol, from which it crystallized in colorless, leafy plates or scales. After two recrystallizations it melted to a clear oil at 257°–258°.

	Calculated for $C_{12}H_{12}ON_2S$.	Found. I.	II.
N	12.07	12.12	12.13

In another experiment, 20 grams of benzylacetoacetic ester gave 13.1 grams of the condensation product, or 62.4 per cent of the calculated.

[1] Ann. Chem. (Liebig), **187**, 12 (1875).

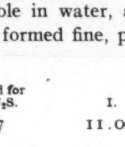
2-Ethylmercapto-4-methyl-5-benzyl-6-oxypyrimidine,



—The above 2-thiouracil derivative was dissolved in alcohol containing one molecular proportion of sodium ethylate and then allowed to digest with a slight excess of ethyl bromide until the solution was neutral. The product, which was almost insoluble in water, and soluble only with difficulty in cold alcohol, formed fine, prismatic needles melting sharply at 166°.

	Calculated for $C_{14}H_{16}ON_2S$.	Found. I.	II.
N	10.77	11.00	10.56

4-Methyl-5-benzyluracil,



—Two grams of the above mercapto compound were allowed to digest for 24 hours on the steam bath with 50 cc. of concentrated hydrochloric acid. Mercaptan escaped, and, on cooling, 1.6 grams of 4-methyl-5-benzyluracil, or 96 per cent of the calculated, separated. The substance was recrystallized from water and alcohol. It gave diamond-shaped plates melting to a clear oil at 249°–250°.

	Calculated for $C_{12}H_{12}O_2N_2$.	Found.
N	12.96	13.06

2-Benzylmercapto-4-methyl-5-benzyl-6-oxypyrimidine.—This was prepared by benzylating 2-thio-4-methyl-5-benzyluracil with molecular quantities of benzyl chloride and sodium ethylate in alcoholic solution. It is nearly insoluble in water. From alcohol it separates in matted masses of long, colorless needles and it melts to a clear oil at 194°.

	Calculated for $C_{19}H_{18}ON_2S$.	Found. I.	II.
N	8.69	8.58	8.75

This benzylmercapto compound proved to be very stable when boiled with hydrochloric acid. It was not desulphurized when given the same treatment as that in the case of the corresponding ethylmercapto derivative. When boiled with hydrobromic acid it was finally desulphurized and 4-methyl-5-benzyluracil was obtained. In view of this behavior it is therefore not a matter of indifference what mercapto derivative is chosen for these desulphurizations.

NEW HAVEN, CONN.,
May, 1909.

ON THE THEORY OF INDICATORS AND THE REACTIONS OF PHTHALEINS AND THEIR SALTS.

BY S. F. ACREE AND E. A. SLAGLE.

[THIRD COMMUNICATION ON THE TAUTOMERISM OF PHTHALEINS.[1]]

(We are indebted to the Carnegie Institution of Washington for aid in our work on tautomerism.)

The rapid advance in our knowledge of the constitution and reactions of colored compounds of the aromatic series has made it clear that we must seek the cause of the manifestation of color in some deep-seated change in the molecule itself. The view formerly held that the color of these particular benzene derivatives is a function only of the increase in the molecular weight, or depends upon the introduction of certain elements or groups which tend to produce color, has long been abandoned.

The first important attempt to formulate a theory of color is seen in the hypothesis of O. N. Witt,[2] brought out in 1876, in which he assumed in all colored compounds the presence of certain specific groups (nitro, azo, cyan, etc.) which were thought to be responsible for the color. Witt called these groups *chromophores*. He recognized in some cases the additional influence of certain salt-forming groups (hydroxyl, amino, etc.) which intensify the color of the chromophore

[1] THIS JOURNAL, **37**, 71; **39**, 528, 789.
[2] Ber. d. chem. Ges., **9**, 522.

and give to the compound the properties necessary in making the dye practically useful. These latter groups were called *auxochromes*.

The quinone theory was first advanced by E. and O. Fischer to explain the colors of the dyestuffs of the rosaniline series and is really an extension of Witt's, which gives a more definite meaning to the term *chromophore*.

In 1889 Nietzki[1] extended the quinone theory, using, however, the modern formula of quinone, to the indamine and azin series. This conception was shortly after extended by Armstrong to include all colored compounds of the aromatic group.

In 1893 Friedländer[2] assigned a corresponding quinone structure to phenolphthalein salts. He accepted Baeyer's formula for phenolphthalein in the free condition,

$$(C_6H_4OH)_2C\begin{matrix}C_6H_4\\ O\end{matrix}CO,$$

but assumed that an intramolecular change takes place in the molecule in the presence of alkalies which results in the formation of the colored quinone salt,

$$NaOOCC_6H_4C(:C_6H_4:O)(C_6H_4ONa),$$

which he assumed to be analogous to the salts of aurin,

$$(NaOC_6H_4)_2C:C_6H_4:O,$$

and of rosolic acid,

$$(NaOC_6H_4)(O:C_6H_4:)C[C_6H_3(CH_3)ONa].$$

As a proof of the existence of the quinone structure in the salt

$$(KOOCC_6H_4)C(:C_6H_4:O)(C_6H_4OK),$$

he prepared an oxime by treating an alkaline solution of phenolphthalein with hydroxylamine. Friedländer also suggested that phenolphthalein is a dibasic acid and that the salts are dibasic salts, but it remained for Meyer and Spengler[3] to prove

[1] Organische Farbstoffe, 1st Edition, p. 2.
[2] Ber. d. chem. Ges., **26**, 172.
[3] *Ibid.*, **38**, 1318.

this by isolating and analyzing the salt $C_{20}H_{12}O_4Na_2$. At about the same time Bernsthen[1] came to similar conclusions in his researches on rhodamine 6 G and suggested that fluorescein exists in the free condition as the lactone compound but has the quinone structure in its salts.

A few years ago another conception of the cause of color was advanced by Baeyer[2] and called by him *halochromy*. He assumed the existence, in colored bodies of the triphenylmethane series, of a peculiar form of valence represented by a wavy bond, C∼∼Cl, which Baeyer and Villiger called the *carbonium valence*. In this condition carbon was assumed to act as a strongly basic element which brings about the manifestation of color. This theory has recently been given up by Baeyer.

In 1890 Ostwald[3] proposed an explanation of color changes based on the theory of electrolytic dissociation. He assumed phenolphthalein to be an extremely weak acid and consequently but little dissociated; on the addition of an alkali a salt is formed which is largely dissociated, and the red color was thought to be due to the anion. The work on the physical constants of phenolphthalein has shown that a close quantitative relationship exists between Ostwald's theory and color change, yet many facts make it evident that this theory is in itself not able to account for all of the known phenomena. While it is true that the negative ions are colored, the change in color is due to a change in constitution of the compound, the ions having a structure different from that of the mother substance.

In 1903 Stieglitz[4] published a valuable article on the theory of indicators. By the use of (*a*) the evidence on the quinone theory furnished by Friedländer and Nietzki, (*b*) Hantzsch's ideas and equations concerning pseudoacids, and (*c*) Ostwald's conception of the quantitative relationships in the indicator work, Stieglitz came to the conclusion, in con-

[1] Chem. Ztg., **1892**, 1956.

[2] Ber. d. chem. Ges., **38**, 570, 1156.

[3] Lehrbuch der allgemeinen Chemie, **1891**, p. 462; Scientific Foundations of Analytical Chemistry, 1890.

[4] J. Am. Chem. Soc., **25**, 1112.

sidering phenolphthalein, that (p. 1115) "its red salts are the salts of a carboxylic acid, *not a phenol*, and have the constitution

$$(MOOCC_6H_4)(HOC_6H_4)C : C_6H_4 : O.$$

The strongly chromophoric quinoid complex ($: C_6H_4 : O$) *gives us an explanation of the production of intense color, which is entirely adequate* in view of the laws governing color in organic compounds." After developing the equation

$$C_Q \times C_H = K'' \times C_{LH}$$

for the affinity constant of the phenolphthalein he stated (p. 1122) that "its tendency to produce *the red color* (*the red salt*)[1] is measured by the same constant K''." Hantzsch[2] points out that he too had proposed this theory.

In 1905 Meyer and Spengler[3] published a very important article in which they showed that the colored salts of phenolphthalein are dibasic salts, but they discarded the quinone hypothesis and accepted Baeyer's theory of halochromy.

In May, 1906, Acree and Brunel[4] began an investigation on indicators as a part of their work on tautomerism. It was seen by them that previous theories did not account fully for either the color phenomena or the alkylation reactions of aurin, phenolphthalein, fluorescein, etc., and they began work on these substances from the point of view that the tautomeric mono- and dibasic phenol and carboxyl salts are concerned in the alkylation reactions and in the color phenomena. It was seen, for instance, as had already been surmised by Friedländer,[5] that *the chief source of color in the salts of aurin, phenolphthalein, etc., is not the quinone group* assumed by practically all of the other workers, but *a quinone-phenolate group*,

$$—C(: C_6H_4 : O)(C_6H_4ONa);$$

$$(KOOCC_6H_4)C(: C_6H_4 : O)(C_6H_4OK);$$

$$(KOC_6H_4)C(: C_6H_4 : O)(C_6H_4OK).$$

[1] All the italics and words in parentheses are ours for emphasis.

[2] Ber. d. chem. Ges., **39**, 1090. Rohland: *Ibid.*, **40**, 2172.

[3] *Ibid.*, **38**, 1318.

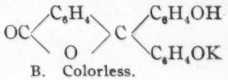
[4] This Journal, **37**, 71. See also *Ibid.*, **27**, 118; **31**, 185; **32**, 606; **37**, 361; **38**, 1; **39**, 124, 226; Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199.

[5] Ber. d. chem. Ges., **26**, 172.

It was clear that the four possible mono- and dibasic salts, A, B, C and D, must be represented as follows:

$(KOOCC_6H_4)C(:C_6H_4:O)(C_6H_4OH)$

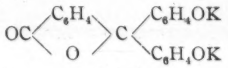
A. Faintly colored.



B. Colorless.

$(KOOCC_6H_4)C(:C_6H_4:O)(C_6H_4OK)$

C. Deeply colored.



D. Colorless.

The compound A, assumed by others to be the colored salt of phenolphthalein, can give only faintly colored solutions, the carboxylphenoldibasic salt, C, being the salt really chiefly responsible for the color changes. B and D were thought to be colorless, as are the corresponding esters. This was perfectly apparent from the work of Nietzki and Burckhardt and Schroeter[1] on the fluorescein and phenolphthalein derivatives, and from the long known work on rosolic acid and aurin, which was pointed out by Friedländer; but the significance of these facts was unfortunately entirely overlooked by the other workers who referred to these articles, a fact which shows that even the most brilliant human minds are very imperfect instruments for aiding us to interpret nature's phenomena. The faintly colored carboxyl ester of tetrabromphenolphthalein, which is already a quinone,

$$(C_2H_5OOCC_6H_4)C(:C_6H_2Br_2:O)(C_6H_2Br_2OH),$$

forms a deeply colored blue potassium or silver salt,

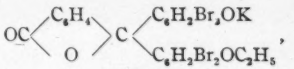
$$(ROOCC_6H_4)C(:C_6H_2Br_2:O)(C_6H_2Br_2OK).$$

On the other hand, the isomeric phenol ester, which according to the quinone theory should yield deeply colored salts, gives practically colorless salts,

[1] Ber. d. chem. Ges., **28**, 48; **30**, 178.

$(KOOCC_6H_4)C(:C_6H_2Br_2:O)(C_6H_2Br_2OC_2H_5) \rightleftharpoons$

Faintly colored.



Colorless.

because no quinonephenolate group can be formed. Especially, though, was this point made clear by the properties of aurin, $(HOC_6H_4)_2C(:C_6H_4:O)$. This compound has already a quinone group, and yet when alkali is added to an aqueous solution of the substance there is formed an intensely colored salt,

$(HOC_6H_4)(KOC_6H_4)C(:C_6H_4:O)$ or $(KOC_6H_4)_2C:C_6H_4:O.$

These reactions were sufficient to show us that the quinone theory alone can not account for the color phenomena. Our view has been recently confirmed more fully by the fact observed by Green and King[1] that the faintly colored carboxyl ethyl ester of phenolphthalein, itself a quinone derivative,

$$(C_2H_5OOCC_6H_4)C(:C_6H_4:O)(C_6H_4OH),$$

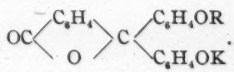
yields the intensely colored *quinonephenolate salt*,

$$(C_2H_5OOCC_6H_4)C(:C_6H_4:O)(C_6H_4OK),$$

whereas the isomeric phenol ethyl ester of phenolphthalein, which *can* form a quinone, but not a quinonephenolate, yields a colorless salt:

$(KOOCC_6H_4)C(:C_6H_4:O)(C_6H_4OR) \rightleftharpoons$

Faintly colored.

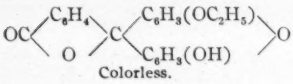


Colorless.

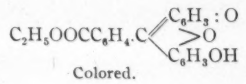
The evidence is just as strong that both phenol and carboxyl salts must be concerned in the alkylation reactions. Nietzki and Schroeter found that their "Fluorescein Kalium" and ethyl bromide gave the isomeric colorless phenol and col-

[1] Ber. d. chem. Ges., **40**, 3724.

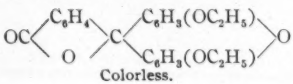
ored carboxyl monoethyl esters, and the isomeric colorless diphenol diethyl ester and colored carboxylphenol diethyl ester:



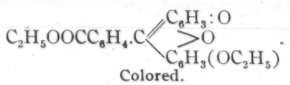
Colorless.



Colored.



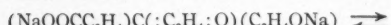
Colorless.



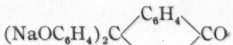
Colored.

These esters seemed from the description given to be stable compounds which did not rearrange, and from Acree's theory of tautomeric compounds it seemed hardly likely that they were formed from tautomeric monobasic salts, but altogether probable that they were obtained from tautomeric dibasic fluorescein salts. Likewise alkylation experiments by Haller and Guyot[1] and by Herzig and Meyer[2] with phenolphthalein salts yielded 85 to 90 per cent of the colorless lactone dimethyl ester, whereas Orndorff[3] found that gallein yields both quinone and lactone esters.

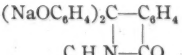
Both the color phenomena, then, and the alkylation reactions pointed to the presence and reactions of tautomeric dibasic salts:



A. Colored.



B. Colorless.

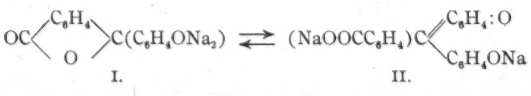


C. Colorless.

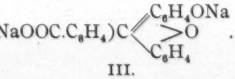
[1] Compt. Rend., **130**, 296.
[2] Ber. d. chem. Ges., **28**, 3258.
[3] This Journal, **31**, 97.

We believed that A is intensely colored, but that salts analogous to B are colorless, just as the corresponding salts of the anilides,[1] C, are without color. But we thought that by "Fluorescein Kalium" Nietzki and Schroeter perhaps meant the *mono*potassium salt, and if this had been true it would have been very unfortunate for our theory. We accordingly ordered some "Fluorescein Kalium" from Hoeschst and Company and the analysis proved that it contained more than 3 atoms of potassium to one molecular quantity of the salt. There was evidently, therefore, justification for a continuance of the problem from our point of view of tautomeric salts, but the work was given up on account of the departure of Dr. Brunel from this laboratory.

In the meantime, other work was appearing which had a very direct bearing on this problem. From a large number of investigations it appeared probable to us that we might have not only the quinoid and lactoid dibasic salts concerned in the colors, but also still another tautomeric salt, an intramolecular condensation product of the phenol salt with the carbonyl of the quinone group, which indeed seemed to be the chief source of color in such compounds:



I. II.

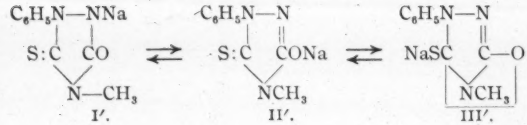


III.

In work begun in 1902, Acree[2] obtained evidence that the 1-phenyl-3-oxy-4-methyl-5-thiourazole and its salts could exist not only in the two tautomeric forms, I'. and II'., ordinarily assumed, but also in still another intramolecular form, III'., analogous to III.:

[1] Meyer and Spengler: Ber. d. chem. Ges., **36**, 2949.

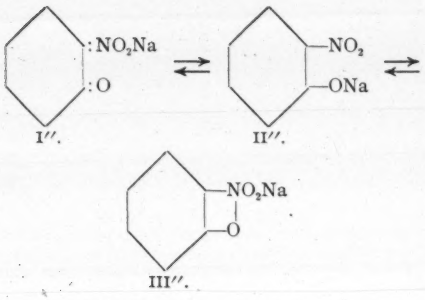
[2] This Journal, **31**, 187; **33**, 606. Nirdlinger: Dissertation, Johns Hopkins University, 1909.



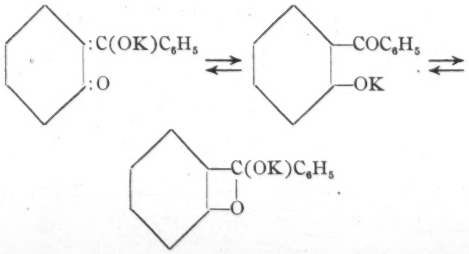
Busch and Opfermann[1] later actually isolated the corresponding 1,4-diphenyl-5-thiourazole acids, and Busch and Reinhardt[2] showed that the salts can exist. Acree and Nirdlinger have now made these tautomeric salts and actually proved quantitatively that one of them has the properties expected of a compound having the structure III′. Although these salts are not visibly colored yet they will without doubt be found to have different colors outside the visible spectrum, as do many other such compounds (Baly, Hardley, Keyser, etc.). The actual isolation of III′. proves the possible existence of the analogous substance III., and as long ago as 1904[3] we pointed out that such intramolecular salts must be considered in addition to the ordinary forms.

Hantzsch,[4] in working on this problem of the cause of color in salts, had to assume, as we were doing, that both forms of the tautomeric acids are ionized, and consequently had to give up his former idea that a tautomeric acid exists in two forms, one of which, the pseudoacid, is not ionized, while the other, the "echt" acid, is dissociated. This led him then to assume the presence of two salts in equilibrium, as we have been doing, instead of the one salt, that of the "echt" acid. But a new idea advanced by him was that there were not only *two* tautomeric salts of nitrophenol, for instance, but also another intramolecular salt, III″., analogous to III., with a different color and different properties:

[1] Ber. d. chem. Ges., **37**, 2333.
[2] Reinhardt: Dissertation, Erlangen, 1906.
[3] This Journal, **31**, 187; **32**, 606, footnote.
Ber. d. chem. Ges., **39**, 1084; **40**, 333.



In another case Hantzsch[1] assumed the presence of such an intramolecular salt, analogous to III. He found that oxybenzaldehydes and oxybenzophenones yield different colored salts to which he gave the formulas



The chief reason, however, for believing that an intramolecular salt, III., is probably the chief source of color in the phenolphthalein series came from work by Jackson[2] and his coworkers, by Wichelhaus[3] and by Posner.[4] Jackson and Oenslager[5] and Clarke,[6] and also Wichelhaus, showed

[1] Ber. d. chem. Ges., **39**, 1084, 3080; **40**, 335. footnote, etc.
[2] Their articles did not bear especially on indicators.
[3] Ber. d. chem. Ges., **5**, 849.
[4] Ann. Chem. (Liebig), **336**, 85.
[5] This Journal, **18**, 1.
[6] *Ibid.*, **34**, 441.

that when a quinone adds sodium phenolate or sodium β-naphtholate, or dimethylaniline, the intensely colored double salts,

$C_6H_4(ONa)_2(OC_6H_5)_2$, $C_6H_4(ONa)_2(\beta\text{-}OC_{10}H_7)_2$,
$C_6Br_4O_2.C_6H_5N(CH_3)_2$, $C_6Cl_4O_2.C_6H_5N(CH_3)_2$,

are formed in *nonaqueous* solvents. Posner ascribed to these compounds different constitutions, but that question does not affect our theory. It was therefore a question to be decided by experiment whether the quinone group and the sodium phenol group of II. might not also combine to form a deeply colored salt, III., even in *aqueous* solutions. But it was clear that the experiments would actually have to be done in aqueous solutions, in which the color changes of phenolphthalein manifest themselves, especially as Jackson found the quinonephenolate addition products to be decomposed by water.[1]

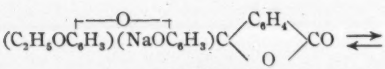
In a similar way it is clear that the phenol ester salt B, p. 126, can not be deeply colored. Since the phenol *esters* do not unite with quinones at all, the color of B is simply that of the quinone group.

If our theory of tautomeric salts is to explain the alkylation reactions and the color changes of phenolphthalein, etc., correctly, three things must be proved *quantitatively*, and to this part of the problem we have now devoted ourselves.

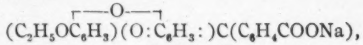
I. It must be proved by experiment that fluorescein forms the tautomeric dibasic salts, each of which yields, to some extent, its corresponding ester in independent side reactions, no ester being formed entirely by a rearrangement of another ester.

We have now been able to do this in a clear-cut way, as is brought out fully in the experimental portion. The phenol ethyl ester of fluorescein, for instance, forms a monosodium salt which is colored and which exists in the two forms in equilibrium with each other:

[1] Jackson and Oenslager: THIS JOURNAL, **18**, 16, 20.

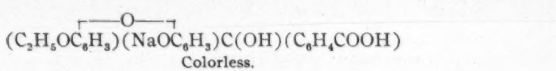


A. Colorless.



B. Colored.

and with their hydrated forms,



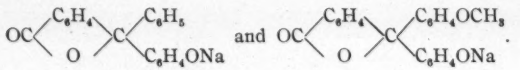
Colorless.

Colorless.

and perhaps with the intermolecular salts.

That there is not simply one salt, B, is proved by the fact that this sodium salt and ethyl iodide yield *two* diethyl esters, the colored quinone ester corresponding to B and the colorless diphenol ester corresponding to A. These esters do not rearrange into each other under the conditions of the experiment and hence at least two tautomeric salts must be present.

This theory of tautomeric salts accounts very nicely also for the *lack of color* in some of these salts. Such substances as *p*-oxydiphenylphthalid,[1] the phenol ethyl ester of phenolphthalein,[2] and the corresponding phenol ester of tetrabromphenolphthalein,[3] dissolve in alkalies without color. Since each of these compounds yields *only* the corresponding lactone ester we believe that the salts have to some extent the lactoid form,



This may be in equilibrium with the hydrated form,

$$(CH_3OC_6H_4)(HOC_6H_4)C(OH)(C_6H_4COONa),$$

[1] Baeyer: Ann. Chem. (Liebig), **354**, 171.
[2] Ber. d. chem. Ges., **40**, 3728.
[3] *Ibid.*, **30**, 177.

which Green and King[1] assumed to be the structure of all these colorless salts. But we do not think that this point of view of Green and King accounts for the formation of nearly quantitative yields of the phenol dimethyl ester from methyl iodide and the sodium salts of phenolphthalein and hydroquinonephthalein, of the phenyl methyl ester of dibrom-*p*-oxydiphenylphthalid from the sodium salt and methyl iodide, or for the formation of *both* isomeric esters of fluorescein obtained by us: our theory does account for these facts. Since Green and King assume the presence of a hydrated *carboxyl salt* we should certainly expect to obtain some carboxyl ester if their theory is correct; but no carboxyl ester is formed, apparently, from the colorless salts mentioned above. It is unfortunate that no one has isolated these colorless salts and shown by analysis whether they are hydrated and become colored when dehydrated, or whether the carboxyl esters rearrange into phenol esters. That these salts may actually exist in the lactoid form is proven, it seems to us, by the fact that Meyer and Spengler[2] actually made the colorless lactoid salts of the anilides of phenolphthalein and hydroquinonephthalein. This is a very important phase of our work and it will be continued in this laboratory from several points of view.

II. It must be proved that these *quinonephenolate double salts* of Jackson and Oenslager and of Wichelhaus and the quiaminones of Jackson and Clarke are formed in *aqueous solutions*. If these were decomposed completely into their constituents in water, it is evident that these substances could not be concerned in the color changes of indicators and dyestuffs as they are ordinarily used. We[3] have fortunately been able to prove that deeply colored compounds are formed by the union of benzoquinone or anthraquinone with salts of *o*-cresol, *p*-cresol, phenol, hydroquinone, pyrogallol and resorcinol, the colors of which disappear when acids are added. In fact such mixtures serve as very good indicators. Likewise, dimethylaniline or α-dimethylamino-

[1] J. Chem. Soc., **85**, 398; Ber. d. chem. Ges., **40**, 3724.
[2] Ber. d. chem. Ges., **36**, 2949.
[3] Acree and Slagle: THIS JOURNAL, **39**, 534, 535.

α-bromnaphthalene and quinone form intensely colored *quinaminones* in aqueous solutions, the color of which fades to that of the quinone when the amine is converted into the salt.

This idea is further borne out by the fact that Bistrzycki's diphenylquinonemethane,[1] which can not form the quinonephenolate salt, $(C_6H_5)_2C : C_6H_4 : O$, is far less deeply colored than the salts of benzaurin, $C_6H_5C(: C_6H_4 : O)(C_6H_4ONa)$, or aurin, $(NaOC_6H_4)_2C : C_6H_4 : O$, which can form the intramolecular, deeply colored quinonephenolate group.

Further evidence is furnished by the brilliant work of Baeyer,[2] who showed that salts of *p*-aminotriphenylcarbinol, $(C_6H_5)_2C : C_6H_4 : NH_2Cl$, which can not form a *quinaminone*, are only light orange in color, whereas the *p,p*-diaminotriphenylcarbinol gives salts having an intense violet color because it forms, to some extent, the deeply colored *quinaminone* group:

$$(NH_2C_6H_4)(C_6H_5)C:C_6H_4:NH_2Cl$$

$$(\overline{NH_2C_6H_4})(C_6H_5)C:C_6H_4:NH_2Cl.$$

When an excess of acids is added to fuchsin or to malachite green[3] the colors fade because the acid converts the amino group into a salt which can not form the quinaminone.

III. The equations and ideas used by Hantzsch and Stieglitz to express the affinity constant of the indicator and the tendency to form the colored salts are not complete[4] and have been replaced by those developed by Acree[5] to show the relations between the equilibrium constants and the affinity constants of the several tautomeric forms of the acid. These equations have been tested experimentally in the urazole series by Acree and Shadinger[6] and found to hold, and

[1] Ber. d. chem. Ges., **36**, 2337.

[2] Ann. Chem. (Liebig), **354**, 161–2.

[3] Acree and Slagle: THIS JOURNAL, **39**, 536.

[4] Acree: *Ibid.*, **39**, 529. Stieglitz: *Ibid.*, **39**, 652. Wegscheider: Z. Elek. Chem., **34**, 510. Hildebrand: J. Am. Chem. Soc., **30**, 1914.

[5] THIS JOURNAL, **38**, 11, *et seq.*, and many subsequent articles.

[6] *Ibid.*, **39**, 124.

similar ideas are also being used by Wegscheider. A great deal of quantitative work will be necessary to clear up all of these problems connected with the indicators. *The cause of the color*[1] *is probably the inter- or intramolecular change of the various salts into each other, as has been brought out thoroughly by Hartley and Baly.*[2]

In the last year or two a number of others have begun work from our point of view that the chief source of color is not the quinone group but a quinonephenolate group, and that the most important source of the color is probably the intramolecular salt formed by the union of the quinone and the phenolate or aniline derivative. In 1907, Baeyer[3] published a long and valuable article on the dyestuffs, in which he gave up his theory of halochromy in favor of the quinone theory, discussing fully his reasons for doing so. He proposed this quinonephenolate theory and tested it by treating fuchsone and fuchsoneammonium chloride with sodium phenolate and dimethyl-*p*-toluidine, but no colors were obtained. Our experiments, however, gave beautiful color changes.

Stieglitz[4] has also given up his former point of view and now has proposed the quinhydrone hypothesis as a cause of the color changes, including the salts as well.

Willstaetter and Piccard,[5] at about the same time, brought out in a valuable contribution the same quinhydrone hypothesis and applied it in a number of directions.

Recently K. H. Meyer[6] has discussed some of the recent work and ideas and prepared a number of compounds.

Since Acree's first paper was published R. Meyer[7] has presented an important article in which he has changed from Baeyer's theory of halochromy to the quinonephenolate theory which we are using.

Wegscheider[8] too has recently taken up the study of phenol-

[1] THIS JOURNAL. **39**, 537.
[2] J. Chem. Soc., **85**, 1029; **89**, 502, 514; **91**, 426, 1572.
[3] Ann. Chem. (Liebig), **354**, 162.
[4] THIS JOURNAL, **39**, 651.
[5] Ber. d. chem. Ges., **41**, 1458.
[6] *Ibid.*, **42**, 1149.
[7] *Ibid.*, **41**, 2446.
[8] Z. Elek. Chem., **14**, 510.

phthalein from a similar point of view and has obtained results in harmony with our theory.

It is evident then that a number of men have been engaged on work which led them to the same general point of view, which is a very great advance in the theory of indicators and dyestuffs. We do not claim any credit for the very important view advanced by Baeyer, Stieglitz, and Willstaetter that *quinhydrones*, as they are always defined, are concerned in the colors of the free acids. But we do believe that our theory of tautomeric salts accounts more fully for the *colors* of the *salts* and their *alkylation reactions* than the theory of any other workers, and since the salts are the substances of chief importance in the colors and reactions of dyestuffs, the free acids or bases being comparatively insignificant in this respect, we shall continue to devote our attention chiefly to this phase of the subject.

A study of the affinity constants of the indicators from our point of view, of the influence of alcohol in decolorizing the salts, of the influence of salts and acids in intensifying the colors of the dyestuffs,[1] and other problems mentioned in our first article are of very great importance. The salts of weak bases, such as $SnCl_2$, $AlCl_3$, etc., and also acids, seem to form deeply colored double compounds with a number of quinoid and lactoid derivatives. We suspect that in all such cases the basic properties of the oxygen of a quinone group are directly concerned.

FLUORESCEIN.

The melting point method can not be used as a criterion of the purity of fluorescein. It decomposed above 290° without melting. Every precaution was therefore taken in the preparation to obtain a pure substance. Pure phthalic anhydride and pure resorcinol were heated with zinc chloride at 180°. The product was obtained free from resorcinol by washing with several liters of cold water, and was then dissolved in a solution of sodium carbonate and precipitated by sulphuric acid. The fluorescein obtained in this way is

[1] K. H. Meyer: Ber. d. chem. Ges., **41**, 2568. Meyer and Hantzsch: *Ibid.*, **40**, 3479.

bright yellow in color. After it is crystallized a number of times from alcohol it becomes dark red, a darker red than sulphophenolphthalein. When the yellow product is heated in an air bath for five hours at 115° it shows no appearance of red whatever. This bright yellow color is retained even after standing in a glass-stoppered bottle eighteen months.

The Four Ethyl Esters of Fluorescein.

The four ethyl esters of fluorescein were obtained by dissolving fluorescein in alcoholic sodium hydroxide, adding ethyl iodide, and heating under a reflux condenser on the water bath. Different amounts of fluorescein, solvent, and halide were used and the time of alkylation varied from four to twenty-four hours. No definite conclusions were reached as to the amounts of the different esters formed under the different conditions. The best yield of esters however, was obtained by continuing the alkylation eight hours.

After the reaction was over any excess of ethyl iodide was expelled by evaporation and the product was poured into cold water, whereupon the two diethyl esters were precipitated. These were then filtered and carbon dioxide was passed into the filtrate. This precipitated the two monoethyl esters.

The only method found for separating the two monoethyl esters was fractional crystallization from dilute alcohol. After repeated crystallizations the colored carboxyl ester, somewhat more soluble in dilute alcohol than the colorless phenol ester, was obtained with a constant melting point 247°. The colorless phenol ester was found to melt, when pure, at 251°.

The colored diethyl ester was separated from the colorless diethyl ester also by fractional crystallization from dilute alcohol. When pure, the colorless diethyl ester melts at 182°, and the colored diethyl ester at 159°.

As stated above, Herzig and Pollak, on methylating fluorescein salts with *methyl iodide*, obtained chiefly the lactoid esters. We have found, in general, that *ethyl* iodide also produces the lactoid esters in excess, although the ratio of the lactoid to the quinoid varies greatly with the conditions of the experiment and time of alkylation. Quite different

results were obtained with *diazomethane*; Herzig and Pollak obtained with this reagent chiefly the quinoid esters.

We have found that *diazoethane* yields, with an excess of either the red and yellow fluorescein, only the colored quinoid diethyl ester. The product of the reaction, without purification, melts at 157°, only two degrees below the melting point of the pure ester, 159°. When this ester is crystallized from glacial acetic acid it gives the proper melting point.

Preparation of the Pure Sodium Salt of the Phenol Ethyl Ester of Fluorescein.

The pure sodium salt of the phenol ethyl ester was prepared by agitating an excess of the ester with a solution of sodium hydroxide and then filtering the undissolved ester. The filtrate was shaken again with a little of the ester and filtered. The filtrate was extracted with carbon tetrachloride and then evaporated to dryness on the water bath. There is no loss in weight on evaporating this salt to dryness on the water bath, although some of the esters are slightly volatile under these conditions.

The sodium salt of the phenol ester dissolves in water with a color much less intense than that of the fluorescein salt, and in ethyl and methyl alcohol with a very faint color at temperatures from —15° to 0°. This color increases very decidedly as the temperature is raised to 80°, but decreases again as the temperature is lowered.

An attempt was made to study the velocity of ester formation; the equation for the reaction is that of the second order,

$$\frac{x}{t(A-x)} = AK.$$

The concentrations of the sodium salt and ethyl iodide were 0.3 weight normal and volume normal, respectively, in 40 per cent alcohol.

The solution was sealed in a tube and heated in a constant temperature bath at 60°.

In the following table t gives the time in hours, A the number of grams of salt taken, x the amount of ester formed,

and $A-x$ the amount of unchanged salt. AK is the constant calculated for a bimolecular reaction.

t.	*A.*	$A-x$.	*x.*	*AK.*
2	0.382	0.3169	0.0651	0.10
3	"	0.3053	0.0767	0.19
4	"	0.2492	0.1328	0.13
7	"	0.2028	0.1792	0.12
(17)	"	0.0190	0.3630	0.11
(24)	"	0.0544	0.3276	(0.25)

The divergence of AK from a constant value is due to the difficulty in obtaining quantitative methods of separation and analysis.

We found that on ethylating the sodium salt as above, a mixture of the colorless phenol diethyl ester and the colored quinone diethyl ester is formed. To separate and identify these esters we boiled the alkylation product about three hours in alkali, which saponified the colored quinone diethyl ester. The solution was then filtered, the filtrate acidified, the phenol ethyl ester extracted with carbon tetrachloride, and identified by its melting point, 247°.

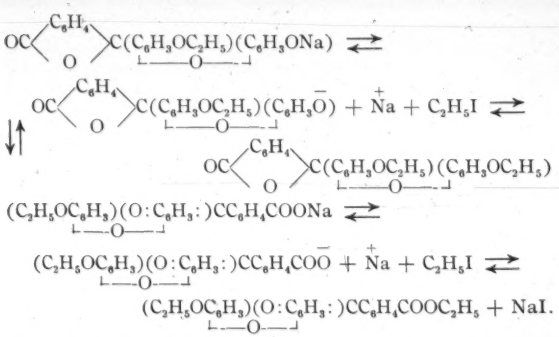
The unsaponified colorless phenol diethyl ester was collected from the filter and identified by the melting point, 251°.

In order to determine whether any rearrangement of the esters took place under the conditions of the experiment, we dissolved 0.0524 gram of the colorless phenol ester and 0.5500 gram of the colored quinone ethyl ester in 5 cc. of 40 per cent alcohol with ethyl iodide in 0.3 N solution of 40 per cent alcohol and heated the mixture a number of hours in a sealed tube in the bath at 60°. The tube was then opened and after separation 0.0516 gram of the colorless phenol ethyl ester and 0.5494 gram of the colored quinone ethyl ester were recovered. We then dissolved 0.6024 gram of the sodium salt of the phenol ethyl ester, 0.0316 gram of the colorless phenol ethyl ester, and 0.1702 gram of the colored quinone ethyl ester in 40 per cent alcohol, sealed this solution in a tube, and heated at 60° for six hours. The tube was then opened and the esters extracted from the salt. After

the separation 0.0306 gram of the colorless phenol ethyl ester and 0.1698 gram of the colored quinone ethyl ester were recovered.

Conclusions from the Alkylations.

Since the colorless phenol diethyl ester and the colored quinone diethyl ester are formed from the sodium salt of the phenol ethyl ester and since we have found that no rearrangement takes place under the conditions of the experiment, the equilibrium and reactions can be expressed as follows:



The equilibrium is assumed to be between the molecular forms of the salts because the evidence obtained in work on the urazoles seems to point in this direction. The same is true of the assumption of a reaction between the alkyl halide and the anions of the salt. We have shown in work in other fields that reaction mechanisms are sometimes very complex and we do not commit ourselves finally as to the above assumptions.

PHENOLPHTHALEIN.

Phenolphthalein was obtained quite pure, melting at 254°, by the method of McCoy.[1]

[1] THIS JOURNAL, **31**, 507.

The attempt to obtain the four esters of phenolphthalein in sufficient quantity and purity by direct alkylation of phenolphthalein in alkaline solution with ethyl iodide proved fruitless. The potassium salt of phenolphthalein was treated with sulphonyl chloride. The reaction was vigorous, sulphur dioxide being evolved. The product of the reaction, resembling tar, was readily soluble in ether and gave a purple color with alkali but was not obtained pure.

TETRABROMPHENOLPHTHALEIN.

Since the tetrabromphenolphthalein and its derivatives were more readily obtained pure, attention was directed to them.

Phenolphthalin was prepared according to the directions of Baeyer.[1] This can be obtained quite free from phenolphthalein by crystallization from boiling water: 100 parts of water dissolve at 20° 0.0175 parts of phenolphthalin. When pure it melts at 225° and dissolves in alkali entirely without color. It is not changed appreciably on standing, but by prolonged heating in air it is oxidized to phenolphthalein.

In all of the following solubility experiments a known quantity of the acid or ester was shaken in a machine with a known quantity of alkali, not sufficient for solution, at 20°, for a number of hours. The undissolved acid or ester was filtered and weighed. The filtrate was acidified and the precipitated material also weighed as a check.

Meyer and Spengler[2] found that the unsubstituted phthaleins neutralize two molecular equivalents of alkali. Our results with the phthaleins verify this. But the phthalins require, in general, somewhat less than two molecular equivalents of alkali, instead of the calculated three molecules, a proof that the phthalins are much weaker acids whose salts are more greatly hydrolyzed. Since we expect to measure the affinity constants of a large number of these dyestuffs a preliminary study of the hydrolysis constants through a de-

[1] Ann. Chem. (Liebig), **202**, 80.
[2] Ber. d. chem. Ges., **38**, 1327.

termination of the solubilities of these substances in alkalies seemed desirable.

Solubility of Phenolphthalin in Alkali.

Amount of acid dissolved.	Calculated cc. of 0.1 N NaOH, one molecular equivalent to one of acid.	cc. of NaOH required.
1.3205	41.3	29.22
0.4901	15.3	10.78

The small amount of alkali required for the solution of phenolphthalin can be explained by the formation of an acid salt in solution.

We prepared tetrabromphenolphthalin by Baeyer's method.[1] It crystallizes from benzene in colorless short needles which melt at 208°–209°. When exposed to the light in a glass-stoppered bottle for several months it becomes colored light pink, without, however, any change in the melting point.

Solubility of Tetrabromphenolphthalin in Alkali.

Amount of acid dissolved.	Calculated cc. of 0.1 N NaOH, two molecular equivalents to one of acid.	cc. of NaOH required.
0.7614	9.12	7.48
0.4731	7.06	5.49

It appears from this experiment that an acid salt is formed in this case.

The carboxyl ester of phenolphthalin was obtained by passing hydrogen chloride into an alcoholic solution of the acid. This ester crystallizes from dilute alcohol in colorless leaves which melt at 157°–158°. The ester is quite stable, being saponified only to a slight extent by standing overnight in a ten per cent solution of sodium hydroxide.

The carboxyl ester of phenolphthalin was brominated by dissolving it in glacial acetic acid and adding bromine. The tetrabrom product crystallizes from glacial acetic acid and melts at 164°.

[1] Ann. Chem. (Liebig); **202**, 85.

Solubility of the Carboxyl Ethyl Ester of Tetrabromphenolphthalin in Alkali.

Amount of acid ester dissolved.	Calculated cc. of 0.1 N NaOH, two molecular equivalents to one of acid ester.	cc. NaOH required.
0.4804	14.46	15.95
0.3160	9.52	10.58

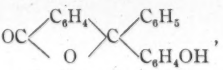
We found that potassium dichromate had no oxidizing effect on this ester. Potassium permanganate and potassium ferricyanide readily oxidize it to the salt of the carboxyl ester of tetrabromphenolphthalein. The free ester was not obtained from this salt in sufficient quantity and purity for the investigation.

We prepared *p*-oxy-*o*-benzoylbenzoic acid according to Friedländer's directions,[1] and the carboxyl ethyl ester by passing hydrogen chloride into the alcoholic solution. The ester crystallizes from glacial acetic acid as a white crystalline powder melting at 115°.

We attempted to bring about the condensation of this ester with phenol in the presence of zinc chloride and also of concentrated sulphuric acid in order to obtain the carboxyl ethyl ester of phenolphthalein, but were unsuccessful.

The attempt to prepare the silver salts of the carboxyl ethyl ester of phenolphthalein and the carboxyl ethyl ester of tetrabromphenolphthalein proved a failure. A water solution of silver nitrate was added to a water solution of each salt at 0° in a vessel of actinic glass, but in each case silver oxide separated and no trace of the silver salt was formed.

p-OXYDIPHENYLPHTHALID.[2]

p-Oxydiphenylphthalid,  , should, from the theory, yield one colorless ester and one colorless salt.

This substance was prepared according to Baeyer's method, by condensing phenol and benzoylbenzoic acid with concen-

[1] Ber. d. chem. Ges., **26**, 172.
[2] Ann. Chem. (Liebig), **354**, 162.

trated sulphuric acid and crystallizing the product from glacial acetic acid. It melted at 164°.

Solubility of p-Oxydiphenylphthalid in Alkali.

Amount of acid dissolved.	Calculated cc. of 0.1 N NaOH, one molecular equivalent to one of acid.	cc. NaOH required.
0.1044	3.46	11.34
0.0700	2.32	7.28

That this acid is extremely weak and the salt highly hydrolyzed is shown by the excess of alkali above the calculated required for solution.

The sodium and potassium salts of *p*-oxydiphenylphthalid are precipitated from a water solution by the addition of an excess of a concentrated solution of sodium or potassium hydroxide but it was found impossible to obtain either of these salts for analysis free from alkali. The attempt to isolate other metallic salts also proved futile.

A colorless oil was formed by heating a solution of the *p*-oxydiphenylphthalid in absolute alcohol with sodium wire but was not obtained pure. No salt was formed on boiling a solution of the acid in anhydrous ether with sodium wire for five hours.

We experienced the same difficulty in attempting to isolate the alkali salts of benzo-*p*-cresophthalein.

On methylating *p*-oxydiphenylphthalid with methyl iodide and alcoholic sodium hydroxide a colorless ester was obtained, but not in pure condition.

DIBROM-*p*-OXYDIPHENYLPHTHALID.

p-Oxydiphenylphthalid was dissolved in glacial acetic acid, at about 60°, and a solution of bromine in glacial acetic acid was added. On cooling the solution, the dibrom-*p*-oxydiphenylphthalid separated out. On crystallization from acetic acid this was obtained pure in white crystals which melt at 199°.

The methyl ester prepared with diazomethane gave on analysis the following results:

	Calculated for $C_{21}H_{18}O_3Br_2$.	Found. (Carius method.)
Br	33.75	I. 33.48
		II. 33.24

Dibrom-*p*-oxydiphenylphthalid was methylated by alcoholic sodium hydroxide and methyl iodide. The methyl ester was obtained as a white powder which crystallizes readily from glacial acetic acid and melts at 157°.

By methylating the dibrom-*p*-oxydiphenylphthalid with diazomethane an identical ester was obtained, melting at 157°. No lowering of the melting point was produced on fusing a mixture of these esters.

These experiments seem to prove very clearly that the sodium salt and the free acid have the same constitution, that of the lactoid form, and give evidence that our theory of tautomeric salts is correct.

EXPERIMENTS WITH THE DILATOMETER.

It seemed likely that the affinity constants of these weak acids might be determined by the use of the dilatometer,[1] provided no salt effect interferes. This method depends on the reversible reaction involved in the condensation of acetone, and the splitting of the diacetone alcohol thus formed into two molecules of acetone. The expansion of the solution due to the change of the diacetone is generally measured. This reaction is catalyzed by the presence of hydroxyl ions and the velocity is proportional to the concentration of these ions.

The diacetone alcohol was prepared by extracting pure calcium hydroxide in a Soxhlet extractor with acetone, according to Hofmann's method. The solution was freed from water and acetone by distilling it under diminished pressure and was then fractionated. The solutions measured contained from two to ten per cent of the diacetone alcohol in conductivity water. A solution of diacetone alcohol in conductivity water showed no appreciable change after standing several months. The measurements were made in a constant tem-

[1] Koelichen: Z. physik. Chem., **33**, 132.

perature bath at 25°. The variation during the experiment was only 0°.01.

Velocity constants for sodium hydroxide having a concentration of N/10, N/20, N/40, N/80, and 160 in theN/ dilatometer were obtained from the equation for the reaction of the first order, $\frac{A}{t(A-x)} = K$. The results are given in Tables I.–V., inclusive.

Equal volumes of ten per cent diacetone alcohol and alkali of the proper strength to give the above concentrations were used. In the tables t is the time in minutes, A the total expansion in divisions on the dilatometer stem, and K the velocity constant.

Table I.—0.1 N Sodium Hydroxide. A = 68.1.

t.	A−x.	K.	t.	A−x.	K.
10	40.0	0.0224	30	14.2	0.0224
15	30.8	0.0226	40	8.4	0.0225
20	24.2	0.0221	50	4.8	0.0224
25	18.4	0.0223			

Mean, 0.0224

Table II.—0.05 N Sodium Hydroxide. A = 36.0.

t.	A−x.	K.	t.	A−x.	K.
5	31.3	0.0119	50	9.6	0.0115
15	23.9	0.0116	55	8.5	0.0114
25	18.4	0.0117	85	3.8	0.0114
35	13.9	0.0118			

Mean, 0.0116

Table III.—0.025 N Sodium Hydroxide. A = 44.2.

t.	A−x.	K.	t.	A−x.	K.
30	29.5	0.00585	100	12.0	0.00575
40	25.7	0.00589	120	9.4	0.00572
60	20.0	0.00574	150	6.4	0.00577
80	15.5	0.00571			

Mean, 0.00578

Table IV.—0.0125 N Sodium Hydroxide. A = 41.2.

t.	A−x.	K.	t.	A−x.	K.
10	38.6	0.00273	100	22.6	0.00271
30	34.2	0.00270	130	19.0	0.00269
50	30.2	0.00270	160	16.0	0.00270
70	27.3	0.00270			

Mean, 0.00270

Table V.—0.00625 N Sodium Hydroxide. A = 48.0.

t.	*A* − *x.*	*K.*	*t.*	*A* − *x.*	*K.*
20	45.5	0.00117	200	29.0	0.00119
50	41.9	0.00118	260	24.8	0.00110
80	38.9	0.00116	320	21.5	0.00119
140	33.5	0.00112			

Mean, 0.00116

Dilatometer Measurements of Solutions of Phenolphthalein.—The pure sodium salt of phenolphthalein was prepared by shaking an excess of the acid with alkali a number of hours and carefully filtering out the excess of acid. A portion of the filtrate containing 0.400 gram of the disodium salt was placed in the dilatometer with an equal volume of ten per cent diacetone alcohol. In Tables VI. and VII., *A* has been calculated only approximately from a number of experiments.

Table VI.—A = 100.

t.	*A* − *x.*	*K.*	*t.*	*A* − *x.*	*K.*
1480	92.6	0.000022	3280	83.5	0.000023
1900	89.6	0.000022	4150	80.8	0.000022
2620	87.6	0.000023	4900	78.1	0.000021

Mean, 0.000022

Table VII.—A = 100.

t.	*A* − *x.*	*K.*	*t.*	*A* − *x.*	*K.*
960	92.9	0.000023	3420	83.6	0.000022
1830	90.2	0.000023	4080	80.6	0.000022
2250	89.4	0.000021	6140	69.2	0.000024

Mean, 0.000022

This volume for K_{trans} corresponds to a hydroxyl ion concentration of 0.00012 N. If we take as the concentration of the phenolphthalein in saturated solution the value 0.0012 N found by McCoy[1] and remember that the solution of the phenolphthalein salt is diluted with an equal volume of the solution of diacetone alcohol, we should obtain 2×10^{-7} for the hydrolysis constant, or 0.6×10^{-7} for the affinity constant of phenolphthalein. This is much larger than the values ob-

[1] THIS JOURNAL, **31**, 511.

tained by Salm, McCoy, Hildebrand, and Wegscheider and shows most decidedly, as do Tables VIII. to XI., inclusive, that the phenolphthalein salt lowers the catalytic effect of the hydroxyl ions very materially. Unless we can find some means to obviate this the method can not be used to determine the affinity constants of these indicators and related compounds.

Solutions of phenolphthalein were then prepared by dissolving a definite amount of the acid in a sodium hydroxide solution containing varying amounts of the alkali. Dilatometer measurements were made with these solutions. The results are given in Tables VIII. to XI., inclusive. It is seen that the velocity constant decreases with increase in the amount of phenolphthalein present.

In the following tables, the amounts of alkali used are expressed in molecular equivalents for one molecular equivalent of acid:

Table VIII.—4.6 N/40 NaOH. A = 50.5.

t.	*A*−*x.*	*K.*	*t.*	*A*−*x.*	*K.*
10	45.9	0.00424	60	28.2	0.00421
20	41.6	0.00420	80	22.8	0.00421
30	37.8	0.00429	120	15.4	0.00429
40	34.2	0.00423			

Mean, 0.00424

Table IX.—20 N/10 NaOH. A = 34.2.

t.	*A*−*x.*	*K.*	*t.*	*A*−*x.*	*K.*
8	24.2	0.0187	24	12.1	0.0187
12	20.3	0.0188	28	10.2	0.0187
16	17.1	0.0187	36	7.2	0.0187
20	14.5	0.0186			

Mean, 0.0187

Table X.—40 N/10 NaOH. A = 28.8.

t.	*A*−*x.*	*K.*	*t.*	*A*−*x.*	*K.*
12	15.9	0.0215	28	7.3	0.0212
15	13.8	0.0213	38	4.5	0.0212
20	10.9	0.0210	49	3.4	0.0210
24	8.9	0.0212			

Mean, 0.0212

Table XI.—70 N/20 NaOH. A = 34.3.

t.	*A*—*x.*	*K.*	*t.*	*A*—*x.*	*K.*
5	30.0	0.0116	30	15.9	0.0110
10	26.5	0.0112	40	11.5	0.0118
15	23.1	0.0114	50	9.6	0.1009
20	20.6	0.0110			

Mean, 0.0113

Dilatometer Measurements of Solutions of p-Oxydiphenylphthalid.

These solutions were prepared by dissolving the acid in varying amounts of caustic soda. The results of the dilatometer measurements are given in Tables XII. to XIV., inclusive. The same salt catalysis is noticed in this case as with phenolphthalein. This salt catalysis was noticed by Koelichen, who found that some salts acted as negative and others as positive catalyzers.

Table XII.—20 N/10 NaOH. A = 34.8.

t.	*A*—*x.*	*K.*	*t.*	*A*—*x.*	*K.*
8	28.3	0.0112	40	12.4	0.0111
16	23.2	0.0110	56	8.2	0.0112
24	18.7	0.0112	72	5.3	0.0113
32	15.3	0.0111			

Mean, 0.0112

Table XIII.—40 N/10 NaOH. A = 32.3.

t.	*A*—*x.*	*K.*	*t.*	*A*—*x.*	*K.*
5	25.3	0.0212	30	7.7	0.0218
10	19.9	0.0210	40	7.7	0.0218
15	15.5	0.0212	60	2.0	0.0217
20	11.8	0.0218			

Mean, 0.0215

Table XIV.—80 N/10 NaOH. A = 33.6.

t.	*A*—*x.*	*K.*	*t.*	*A*—*x.*	*K.*
5	25.8	0.0229	25	9.0	0.0227
10	19.9	0.0227	30	7.0	0.0228
15	15.1	0.0229	40	4.0	0.0229
20	11.7	0.0229			

Mean, 0.0228

The above results for the various concentrations of sodium hydroxide, phenolphthalein, and *p*-oxydiphenylphthalid are shown in Fig. I., plotted in the form of a curve.

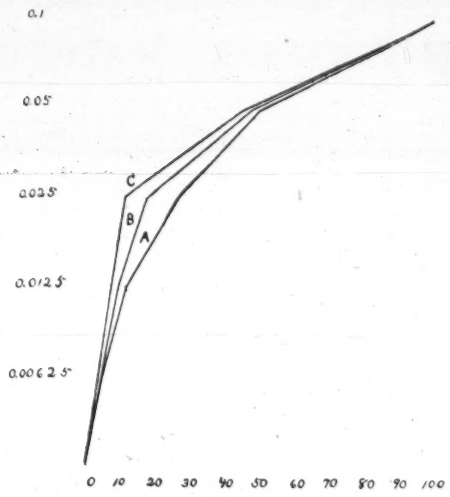


Fig. I.

The abscissas represent the velocity constants, K, and the ordinates the normality of the original alkaline solutions. Curve A shows the results for sodium hydroxide (the deviation of A from a straight line is, of course, due to the suppressed ionization at the higher concentrations); curve B shows the results obtained with the phenolphthalein solutions; and C, those obtained with solutions of *p*-oxydiphenylphthalid. The decrease in the velocity contant due to the presence of the phthalein or phthalid salt is very clearly shown, the decrease being greater in the case of *p*-oxydiphenylphthalid, C, than in the case of phenolphthalein, B.

A New Dilatometer.

It is readily seen that the glass dilatometer as devised by Koelichen is not sufficiently sensitive for studying very dilute solutions of alkali nor for the very accurate investigation of this salt catalysis. An attempt was made to obtain a more sensitive instrument by following the plan used by Prof. Morse in his work on osmotic pressure.

A brass cell (Fig. II.) was made, with a capacity of 25 cc. and an internal diameter of 17 mm., the wall being 2 mm. thick. The cell was uniformly nickel-plated inside and outside. It was closed by a brass cone (*b*) into which was fastened with Wood's metal (*c*) an open manometer tube, etched in 1 mm. divisions, and having a bore of 0.5 mm. diameter. A small platinum tube (*d*) opening within the cell, by the side of the manometer, was also fastened into the cone. This small tube could be closed with a screw cap (*e*).

The cap was used to regulate the height of the liquid in the manometer before the measurements were taken. When a measurement was to be taken the manometer tube was filled with pure water. The diacetone alcohol and alkaline solution were brought to the proper temperature, thoroughly mixed, and then poured into the cell. The cone containing the manometer was then quickly placed in the cell and tightened by the threaded brass collar (*g*). The superfluous liquid was allowed to escape from the small platinum tube until the meniscus was at the proper height in the manometer tube and the screw cap was then tightly closed. It was found impracticable to use washers of any kind between the cone and the cell at (*f*), as their slightest contraction or expansion caused a change in the volume of the cell and hence an error in reading. A watertight connection was obtained at this point (*f*) by the use of a thin layer of a mixture of vaseline and the lubricant obtained by melting together rubber and paraffine.

During the measurements, which lasted from three to nine hours, the instrument was immersed so that the meniscus was at a constant level in a constant temperature bath. The

temperature must be carefully regulated as a change of more than 0°.005 of a degree causes considerable error in reading.

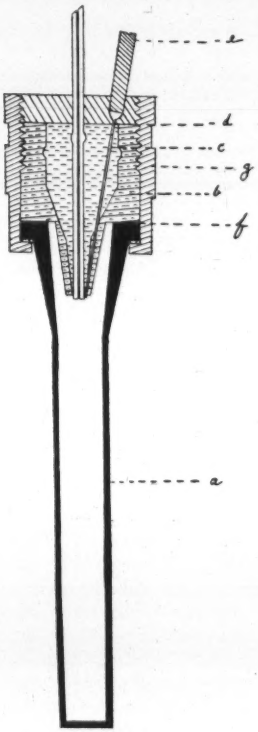


Fig. II.

A number of improvements have suggested themselves while working with this instrument, yet the advantages of the present type over the glass dilatometer are evident. This

cell, when placed in the bath, will attain temperature equilibrium in two to three minutes. The following tables will show the degree of accuracy that can be attained. In these measurements a 2 per cent solution of diacetone alcohol was used.

Table XV.—0.0483 N Sodium Hydroxide. A = 14.29.

t.	$A-x$.	*K.*	*t.*	$A-x$.	*K.*
2	13.57	0.01123	31	6.41	0.01125
4	12.89	0.01120	41	4.95	0.01120
6	12.23	0.01126	51	3.83	0.01123
21	9.32	0.01121	61	2.95	0.01126
26	7.13	0.01126			

Mean, 0.01123

Table XVI.—0.0227 N Sodium Hydroxide. A = 22.90.

t.	$A-x$.	*K.*	*t.*	$A-x$.	*K.*
10	20.10	0.005673	35	14.50	0.005670
15	18.39	0.005677	50	11.92	0.005671
20	17.63	0.005679	60	10.46	0.005672
25	16.52	0.005672	70	9.18	0.005672
30	15.47	0.005678			

Mean, 0.005675

These are remarkably good constants and serve to show how accurate our chemical methods can be made. Doubtless many other reactions can be studied by such methods and we shall continue the work as outlined above.

EXPERIMENTS ON THE RADIOACTIVITY OF ERBIUM, POTASSIUM, AND RUBIDIUM COMPOUNDS.

By W. W. Strong.

The work of Thomson, Campbell, Wood, McClennan, and others has indicated that potassium and probably rubidium are radioactive. McClennan and Kennedy[1] have studied the salts of various metals and find that only potassium salts are appreciably active. Levin and Ruer[2] find that potassium salts emit radiations that are about a thousandth part as

[1] Phil. Mag., **93**, 377 (1908).
[2] Physik. Z., **8**, 248 (1908).

strong as the β rays from uranium. The latter investigators used the photographic method. This method is quite easy and has been used in this work, which is merely a preliminary one. The activity of any of the ordinary elements which has been thus far observed is so small that it could be explained as due to but a minute trace of any of the so-called radioactive elements. No good method has as yet been brought forward to show the absence of any such impurity and the only way we have of settling this important problem is to investigate various kinds of salts of the substance prepared by different methods and from materials derived from as many different sources as possible. For this reason the present work does not prove that erbium, potassium, and rubidium are radioactive, but it indicates that there is considerable evidence that they are.

Several years before his death, Prof. Rowland collected several minerals and salts of the rarer elements, and through the kindness of Prof. Ames these were placed at the writer's disposal. An investigation of the possible radioactivity of these compounds has been made by the photographic method.

The substances examined include salts of potassium, zirconium, caesium, lead, bismuth, yttrium, tungsten, sodium, molybdenum, niobium, rubidium, erbium, tantalum, lanthanum, vanadium, neodymium, praesodymium and ruthenium. Most of the substances were collected by Prof. Rowland about fifteen years ago and may be considered "old" from a radioactive point of view.

The method of investigation consists of exposing "Seed's Dry Plates" for about six months to the salts. The salt is usually placed in a small dish covered with a screen containing several openings. Above this opening is the photographic plate, the film side being next the salt. As most of the salts had been in cork-stoppered bottles for years, there was usually not much danger of chemical action although in several instances this trouble occurred. Intense impressions were obtained from uranyl compounds for exposures of thirty hours or more.

Of the results obtained, only those are given that indicate that the substance is radioactive.

Potassium salts: Potassium cyanide (purchased for photographic purposes) gave a photographic impression on being exposed 150 days. Thin aluminium foil (0.00156 cm. thick) did not cut off much of the radiation from the salt. Thicker aluminium foil (0.006 cm. thick) absorbed about half the radiation. A sample of potassium benzoate (Row. collection) exposed for 150 days, produced a very slight photographic impression. Potassium citrate (Row. col.) exposed 160 days showed a weak photographic action that was not screened off by thin aluminium foil, but was entirely screened off by sheet iron (0.044 cm. thick). Potassium urate (Row. col.) showed practically no effect after an exposure of 150 days. Potassium carbonate (Row. col.) gave a strong impression after an exposure of 160 days. The radiations were absorbed by sheet iron. On the other hand, potassium carbonate recently purchased for photographic work (Mallinckrodt) showed practically no activity at all. The same was true of potassium chromate (Row. col.) which was exposed 150 days. These results seem to indicate that potassium salts, both the "new" and the "old," are radioactive, and that this activity is not much greater than can be detected by this method. Many commercial salts of potassium (especially potassium cyanide)[1] contain but small amounts of potassium, and would therefore be but slightly active and would require much longer exposures than those given above.

Of the lead compounds investigated, only one, lead peroxide, was slightly active. Metallic lead usually gives very marked photographic effects. These do not appear to be due to a β-like radiation, however, for if the lead is placed a short distance from the plate, the effect is much reduced. The effect may be due to a δ-like radiation. Wood gave effects somewhat similar to those of lead.

A sample of erbium chloride gave a very strong impression after an exposure of 110 days. This salt belonged to the Rowland collection. Several years ago the University pur-

[1] McClennan and Kennedy: Phil. Mag., **93**, 386 (1908).

chased some "erbium metal" from the Harrington Brothers, London. This powdered "metal" also gave a very strong impression. The erbium chloride is known, from the spectroscopic observations, to contain a large amount of erbium. The absorption spectra of the powdered "erbium metal" did not show a trace of the erbium spectrum.

A powder marked "Samarkite oxides" (Row. col.) did not show any activity. Samples of samarkite earths and monazite sand (Barker Co., N. C.) showed indications of marked radioactivity.

Rubidium chloride gave a slight impression and rubidium chlorate a very strong impression after exposures of 110 hours.

Not a single one of the other salts showed the slightest indications of being radioactive. The fact that most of the potassium salts and all of the erbium and rubidium compounds tried gave photographic impressions, indicates a probability that potassium, erbium, and rubidium are radioactive.

JOHNS HOPKINS UNIVERSITY,
June, 1909.

PRODUCTION OF CARBON DIOXIDE FROM SOLUTIONS OF COMPOUNDS OF SILICON, ZIRCONIUM, BISMUTH, AND THORIUM.

BY SIR WILLIAM RAMSAY.

In the following extract from Sir William Ramsay's presidential address, delivered before the London Chemical Society on March 25th, 1909, entitled "Elements and Electrons" and published in the *Journal of the Chemical Society* for April, 1909,[1] are described a number of experiments which lead him to believe that he has effected the transmutation of four other elements, besides copper, into an element of lower atomic weight, *viz.*, of silicon, zirconium, bismuth, and thorium into carbon. He says:

No one is better aware than I am how careful one should be in publishing results; but it has appeared to me best to make public the conclusions to which my experiments have led

[1] Vol. **95**, pp. 624–637.

me; if the experiments are faulty, they will be repeated and corrected; if just, they will be corroborated.

I need here only allude to the transformation of radium emanation into helium, discovered by Mr. Soddy and myself. The accuracy of this observation has been amply established. Owing to the fact that during this transformation the energy evolved is in the most concentrated form known, and that the emanation of radium is fairly easily soluble in water, and therefore in aqueous solutions, the action of the emanation on a solution of copper sulphate and nitrate was investigated, glass vessels being employed. Four experiments were made, each one in duplicate; the duplicate was in each case treated like the solution containing emanation; the only difference was that the duplicate solutions contained no emanation. From the emanation-solutions, a larger residue was obtained in each case than from the duplicate; and while the residue from the emanation-solutions showed the presence of a trace of lithium, those from the duplicates failed to give spectroscopic evidence of the presence of lithium. The fact of the experiments having thus been carried out in duplicate renders inapplicable the criticism of Professor Hartley, that inasmuch as lithium is a widely distributed element, accidental contamination is probable. But the alleged repetition of the experiments of Madame Curie and Mlle. Gleditsch, in which, using platinum vessels, they obtained no greater residue, and no trace of lithium, cannot be thus explained away. There are two possible replies: either the conditions of experiment varied, so that the same result was not obtained; or it is conceivable that in presence of emanation and a copper solution, a trace of lithium was dissolved from the glass vessel (which had been tested for lithium, however, with negative result), which escaped solution in absence of emanation, on the one hand, or in the absence of copper, on the other. For emanation in presence of distilled water in a vessel of the same glass gave a minute residue in which the spectrum of lithium was not to be observed.

I may be permitted here to mention a research carried out by Mr. Alexander Cameron, under my supervision, on the

action of emanation on a solution of silver nitrate in a silica bulb, no glass, but only silica and platinum vessels, having been used for the experiments. Two experiments were made, in which the silver nitrate solution was left over a month in presence of the emanation from 0.2111 gram of radium, reckoned as metallic. Two similar blank experiments were made, in which no emanation was introduced into the bulb. These experiments had the object of ascertaining whether the "treated" silver nitrate gave a larger residue than the "untreated." The utmost pains were taken, it is needless to say, to avoid the introduction of any solid matter with the reagents employed. The results were negative; they are as follows:

	Residue from "treated" silver nitrate.	Residue from "untreated" silver nitrate.
Expt. 1	0.00022	0.00032
Expt. 2	0.00027	0.00007

The differences are so small, and the difficulty of avoiding contamination so great, that no positive conclusion can be drawn from the experiments. It is really impossible to manipulate quantities of the order of a few tenths of a milligram. The residues showed only the spectrum of sodium.

But the available energy of the radium emanation was certainly largely expended in producing another change, for a large amount of metallic silver was deposited—no less than 0.23 gram. Besides this, the gases evolved consisted of: Oxygen, 1.038 cc.; hydrogen, 0.071 cc.; nitrogen, 0.084 cc.; and carbon dioxide, 0.016 cc.;[1] in all, 1.209 cc.

The total amount of emanation with which these solutions were treated was respectively 0.78 and 0.92 of that evolved from a gram of radium in 3.86 days—a comparatively large dose, and one capable of evolving about 5,000 gram-calories.

It is, however, possible that silver is a very "stable" element, and that a bad selection has been made. Judging again by analogy with compounds, if it were required to separate carbon from one of its compounds, it would puzzle a beginner if carbon dioxide were the particular carbon compound fixed

[1] The carbon dioxide was probably due to the grease of the stopcock of the burette in which the explosion was carried out.

on as a source of carbon; while, with cane sugar, mere application of heat would reveal its content of carbon. Only repeated experiment can solve this problem—to discover the less stable, and, therefore, more easily degraded, elements. Probably they should be sought for among those of high atomic weight.

I have, however, stumbled across a case of apparent transformation, in working in a totally different direction. After the demonstration that helium is a transformation-product of radium, Debierne showed that it is also to be obtained from actinium. Naturally, the idea occurred that thorium should also yield helium. Now, the radioactive constant of thorium is only the 1/180,000th part of that of radium; hence the necessity of working with a very much larger quantity, over a very much longer time.

Miss Burke was so good as to purify for me 270 grams of thorium nitrate, $Th(NO_3)_4$. On December 20th, 1905, it was dissolved in about 300 cc. of water, and introduced into a round-bottomed flask, provided with a capillary neck, on which was sealed an excellent stopcock. The stopcock was greased, and after the flask had been evacuated with a Töpler pump, the tap was closed. After some hours, it was again pumped empty, and again left; and this proceeding was repeated at intervals, until absolutely no gas could be pumped off. The thorium nitrate was fairly acid, for unless some free acid is present, it is difficult to avoid its being hydrolyzed by water. After this complete withdrawal of all gas, the glass connection to the Töpler was broken; the upper part of the capillary tube, above the stopcock, was filled with water, and the flask was inverted into a jar of water. During the three years in which the gaseous contents of the flask were under observation no trace of leakage at the stopcock occurred; no water entered. Had leakage occurred, it would have been detected by a line of demarcation in the capillary tube, between the strongly refracting solution of thorium nitrate and the less refractive water.

The flask was left for 168 days, and was then sealed to a Töpler pump, with a U-tube, cooled with liquid air, interposed

between the flask and the pump. On opening connection to the pump, a white substance deposited in the U-tube. As the presence of carbon dioxide was not suspected (the experiment having been made to test for helium), this white deposit was not investigated; there was, however, a suspicion that it might be carbon dioxide. The total volume of gas collected measured 3.523 cc.; it contained 0.061 cc. of explosive mixture of hydrogen and oxygen. The residue was mixed with excess of oxygen, and the nitrogen removed by sparking in presence of caustic potash. The gas remaining was then introduced into a tube containing phosphorus, and the oxygen was removed. The minute residue was forced into a minute capillary vacuum-tube, and its spectrum examined. The tube was nearly phosphorescent; I could not be certain, but I suspected that I saw the yellow line of helium. The flask was treated as before, and set aside for 250 days (June 6th, 1906, to February 11th, 1907). The gas then pumped off was analyzed. Its volume was 5.750 cc.; it contained 0.588 cc. of carbon dioxide, absorbable by potash, and 0.017 cc. of hydrogen plus oxygen; the residue, 5.145 cc., was pure nitrogen. Here the volume of gas emitted from the thorium nitrate was nearly proportional to the time. Again, helium was sought for, but without definite result; the yellow line was doubtful.

After closing the flask as before, it was kept for 173 days, until August 3rd, 1907. The gas, on analysis, gave carbon dioxide, 1.08 cc.; hydrogen and oxygen, 0.02 cc.; and nitrogen, 1.64 cc.; the total volume was 2.74 cc. The testing for helium was very satisfactory as regards manipulation, but the presence of the D_3 line was questionable.

On August 14th, 1907, a control experiment was started, in which a solution of 300 grams of mercuric nitrate, in the minimum quantity of water, was enclosed in a similar flask, pumped empty, and inverted. This salt was chosen because mercury is not supposed to be a radioactive metal, and because of the known oxidizing qualities of mercuric nitrate. The gas withdrawn from this flask on March 30th, 1908, consisted of 0.015 cc. of carbon dioxide, 0.034 cc. of oxygen, and 3.628 cc. of nitrogen. That from the bulb with thorium nitrate con-

tained 1.209 cc. of carbon dioxide, 0.016 cc. of hydrogen and oxygen ($H_2 + O_2$), and it left a residue of 1.321 cc. of nitrogen. After sparking down, there was distinct evidence of a helium spectrum; that is, the D_2 line was observed, but the tube almost at once "ran out." To make certain, however, of the production of helium from thorium, a larger quantity is evidently necessary.

The next analysis was made on February 9th, 1909. It occurred to me that although the grease on the stopcock had been exposed to only a trace of liquid—that in the narrow capillary tube—still, carbon dioxide might have been produced in presence of thorium, although the similar experiment with mercuric nitrate gave a practically negative result. To guard against this, a little metallic mercury was introduced, without letting in a trace of air. When the flask was inverted, the capillary tube was filled with mercury, which effectually protected the stopcock from contact with the thorium solution. On examining the flask on February 9th, 310 days after the gas had been withdrawn, no bubbles could be detected between the stopcock and the mercury; had carbon dioxide risen from the grease, it must have been trapped there.

The result of the presence of this mercury was unexpected. Instead of the 3 or 4 cc. of gas, no less than 180 cc. were collected; analysis of a small portion showed that it was almost pure nitrogen. To extract the carbon dioxide, the whole of this gas was liquefied in a bulb cooled with liquid air, under a pressure of two atmospheres; and the nitrogen was allowed to boil away into a gas-holder. The residue in the bulb was collected separately. The process was repeated a second time. The first small portion of gas contained 0.411 cc. of carbon dioxide; the second, 0.103, in all, 0.622 cc. It is probable, however, that not all was then separated, for carbon dioxide has still a small vapor pressure at $-185°$.

These experiments render it at least probable that thorium nitrate "engenders" carbon dioxide; or, in other words, that one of the degradation products of thorium is carbon.

To test this question further, two quantities of thorium nitrate, carefully purified, were treated with radium-emana-

tion, which had stood for some hours in a tube containing moist potash. It was introduced rapidly into a bulb, and the only chance of contamination with carbon compounds was while it passed through a stopcock on its way to the bulb; the time of contact cannot have been a fraction of a second. A special experiment, to be described elsewhere, has shown that grease, in contact with emanation, yields, when oxygen is absent, nothing but pure hydrogen; not a trace of carbon dioxide.

The first quantity of thorium solution was charged with emanation on June 3rd, 1908; the bulb was opened, and the gas analyzed, on November 18th. Nitric peroxide was present; it was removed by shaking with mercury, some pure oxygen having been added to combine with nitric oxide. The volume of the gas was then 5.579 cc. No electrolytic gas was present, but 0.551 cc. of carbon dioxide, 1.342 cc. of oxygen, and 3.686 cc. of nitrogen. The method of filling this bulb absolutely precluded entry of air at any time. The same solution in the same bulb was recharged with a much smaller quantity of emanation on November 20th; the bulb was opened on February 2nd, 1909. After removal of oxides of nitrogen with mercury as before, the volume was 1.789 cc.; it contained 0.124 cc. of carbon dioxide, 1.026 cc. of oxygen, and 0.639 cc. of nitrogen; there was no electrolytic gas.

From these experiments it would appear that the action of radium emanation on thorium nitrate solutions is also attended with the formation of carbon dioxide. Thorium belongs to the same natural family as carbon; and experiments were next tried with another member of the same family, namely, zirconium. Two bulbs were therefore charged with an acid solution of zirconium nitrate, and each "dosed," on August 19th and 26th, 1908, respectively, with the radium emanation from 0.2111 gram of radium as bromide, gathered during eight days. The gases were analyzed as on the 20th November. After oxides of nitrogen had been removed, the remaining samples had the following composition:

	I.	II.
Carbon dioxide	0.124	0.116
Carbon monoxide	0.002	0.008
Nitrogen	0.456	0.762
Oxygen	3.831	3.665

There was no electrolytic gas.

Having obtained carbon dioxide from zirconium nitrate, hydrosilicofluoric acid was similarly treated with the emanation of a week's gathering from the same quantity of radium. The carbon dioxide from 10.2 cc. of what was practically all electrolytic gas amounted to 0.106 cc. I am much indebted to Mr. Usher for carrying out the analyses of these gases.

To ascertain whether lead, too, yielded carbon dioxide, a bulb was charged with an acid solution of lead chlorate, and dosed with emanation; the bulb was set aside on December 18th, 1908; the gases were extracted and analyzed on January 26th, 1909. The bulb contained a thick deposit of lead peroxide; the gas did not attack mercury, hence there was no free chlorine; it consisted wholly of oxygen, 5.192 cc., and carbon dioxide, 0.007 cc. The amount of the latter gas is here insignificant; and the experiment may be regarded as a blank one as regards the production of carbon dioxide.

A similar experiment was made with bismuth perchlorate, obtained by dissolving bismuth oxychloride in excess of perchloric acid, and evaporating until the solution became syrupy, and until white fumes appeared. Some crystals deposited on cooling. The oxychloride was tested for nitrates and nitrites with brucine; none were present. The pressure in the bulb, on opening, was very high, due to formation of oxygen and chlorine. The total amount of carbon dioxide found was 0.150 cc., and of oxygen about 48 cc. Now, as the solution of bismuth perchlorate had been evaporated until the fumes of perchloric acid were evolved, and as all carbon compounds—dust, etc.—must certainly have been oxidized, the formation of carbon dioxide appears certain. The mercury which had absorbed the chlorine was carefully tested for nitrates, but with negative result; and no nitrogen was present in the gases produced. This may appear curious,

for bismuth belongs to the nitrogen group; but in such matters it would be bold to predict. The fact that nitrogen was absent from the bulbs containing lead and bismuth points to the absence of air, and inferentially also to its absence in the other experiments described. Indeed, it is certain that in all these experiments, all gas was initially extracted from the solutions; and no gas entered during the subsequent manipulations.

Much more might have been said regarding the special precautions taken, For example, a pump with a specially narrow fall-tube was employed; 1 cm. of its length contained about 1 cubic millimeter. The exhaustion of the bulbs was carried so far that no appreciable bubble passed down the fall-tube; 1/100th cubic millimeter could have easily been detected. Again, all vessels were washed out with hydrogen made by heating palladium-hydrogen in connection with a pump; tubes, explosion-burette, measuring-burette, etc., so as to avoid all possible source of contamination. In short, every precaution which could be thought of was taken to exclude all foreign gases. The emanation, besides, before it was introduced into the bulbs, had stood for several hours over moist potassium hydroxide; that treatment had been found repeatedly to exclude all traces of carbon dioxide, for it has been tested for spectroscopically and its absence conclusively proved.

Such are the facts. No one is better aware than I how insufficient the proof is. Many other experiments must be made before it can confidently be asserted that certain elements, when exposed to "concentrated energy," undergo degradation into carbon.

REPORT.

Relation between Crystalline Form and Chemical Constitution.[1]

The relation between crystalline form and chemical constitution is a subject which has long attracted the attention of

[1] Abstract of an article by William Barlow and W. J. Pope published in J. Chem. Soc., **91**, 1150 (1907).

students of chemistry and crystallography. Messrs. Barlow and Pope published an article upon this problem in the *Journal of the Chemical Society*, in 1906, presenting views of fundamental importance which, if supported, lead to far-reaching conclusions. The same authors have since published two articles in which they give many additional facts bearing upon the ideas formerly advanced. Because of the importance of the subject and the significance of their views, it is our purpose to present the chief conclusions reached by the authors in their second article. A review of their last article will appear in a later number of THIS JOURNAL.

In their earlier work, the authors reached two fundamental conclusions, as follows: If each atom be viewed as appropriating a certain space, termed its sphere of atomic influence,[1] then (1) the spheres of atomic influence are so arranged as to occupy the least possible space in every crystal, *i. e.*, they are close-packed; (2) the volumes of the spheres of atomic influence in any body are proportional to the valence of the combining atoms.

A third proposition is now advanced by the authors in addition to the preceding.

(3) In any compound, the volumes of the spheres of atomic influences of atoms of the same valence may differ slightly. In other words, the volumes of equivalent atoms, though approximately the same, may not be absolutely identical.

The latter proposition receives especial consideration in the paper before us.

Method of Investigation.—If the spheres of influence of atoms of the same valence possess the same volume and if the atoms are close-packed in any crystal, as affirmed by the laws previously advanced, it is manifest that crystals formed by combinations of such atoms must possess the properties of close-packed assemblages of equal spheres. The method of the authors, therefore, is to consider first the properties of an ideal assemblage, and then to observe how far the crystal forms assumed by combinations of equivalent atoms accord with those of the ideal assemblage.

The authors consider (I) the ideal assemblages of spheres of equal volume, (II) the crystal form of the various elements,

[1] The authors use the phrase "sphere of atomic influence" to express the space appropriated by the atom, in which respect it is essentially the same as "atomic volume." There appears, however, to be this difference between the terms: the atomic volumes, as commonly determined, express the relative volumes of atoms of the same substance, uniting to form the elementary bodies, while the spheres of atomic influence express the relative volumes of atoms of different elements uniting to form compounds, *e. g.*, the relative volumes of the Na and Cl atoms in NaCl.

and (III) the crystal forms of combinations of equivalent atoms.

I. THE IDEAL ASSEMBLAGES OF CLOSEST-PACKED SPHERES OF EQUAL VOLUME.

Methods of Close-packing.—Two types of closest-packed spheres of equal volume exist, and two only, which may be termed the cubic and hexagonal close-packing, respectively. This may be shown in the following manner: Let the spheres be arranged in contact in one row, as shown in the dotted circles of Fig. I. Let the successive rows be assembled by placing spheres

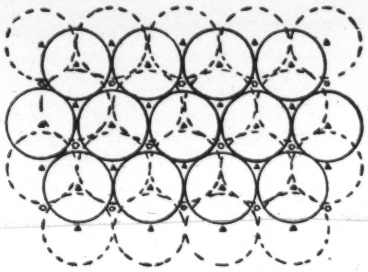


Fig. I.—Projection of hexagonal close-packing seen upon basal pinacoid (0001).

so that they occupy the hollows of the adjoining rows, as shown. The resulting arrangement is the closest-packed assemblage of equal spheres in one plane. Superpose the spheres of a second plane so that they lie in the hollows between those of the first plane, as shown by the solid circles in Fig. I. This gives the closest packing in two planes. The spheres of a third layer may now be superposed in the hollows of the second layer in two different positions:

(1) So that the spheres of the third layer lie immediately over those of the first layer, their centers being in the positions indicated by the small triangular signs in Fig. I.

(2) So that the spheres lie in the intervening hollows indicated by the small hollow hexagons in Fig. I.

These two methods differ in this, that in the first case the spheres of the third layer lie immediately over the spheres of the first layer, while in the second case the spheres of the fourth layer lie immediately over those of the first layer. These are manifestly the only possible ways of closely packing

equal spheres. The resulting structures are illustrated in Figs. I. and VI. and are termed the hexagonal and cubic methods of close-packing, respectively.

One of these arrangements can readily pass into the other by a slight shear in the structure. Thus if the fourth layer of the cubic type slips so as to be over the second layer it will yield the hexagonal arrangement, and *vice versa*.

We will next examine the characteristics of these two assemblages.

Cubic Assemblage of Closest-packed Spheres.

Arrangement of Spheres.—The cubic assemblage of closest-packed spheres may, for the purpose of discussion, be subdivided into cubic cells in which the spheres are close-packed. Of course, such a conception is purely artificial and for the purpose of visualizing the results. There is no such subdivision into cells in nature. Such a cubic cell is outlined in Fig. II. where the observer looks down upon the solid angle of the cube. It is shown, separated from the remaining spheres, in Fig. III. and is viewed from the side in Fig. IV. The cubic cell illustrated contains 5 spheres in each face and may be considered as made of superposed layers of four and five spheres as shown in Fig. IX. A larger cube is illustrated in Fig. V.

The cubic assemblage may also be viewed as made of still smaller units, termed tetrahedra, each tetrahedral group consisting of four spheres occupying the solid angles of a tetrahedron. Their position is shown in Fig. V., in which the spheres of each tetrahedron are inscribed in a small cube. It is important to note that all the tetrahedra have the same orientation, their three-fold axes coinciding with the three-fold axes of the larger cubic cell.

The arrangement of the spheres is shown in greater detail in Figs. VI., VII., and VIII. In these figures, the dotted lines represent the lowest layer, the lighter circles the intermediate layer, and the heavy circles the uppermost layer. Fig. VI. shows the arrangement as seen on the face of the octahedron, Fig. VII. as seen upon the cubic face, Fig. VIII. as seen upon the face of the rhombic dodecahedron.

Symmetry.—Examination of the cubic assemblage shows the following elements of symmetry:

1. *Axes of Symmetry.*

a. Four-fold axes of symmetry pass through the center of each sphere, normal to the cubic face (Figs. VII. and IX.).

b. Three-fold axes of symmetry pass through the center of each sphere, normal to the octrahedral face (Figs. II and VI.).

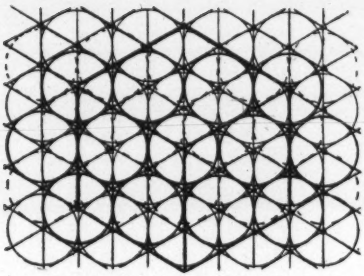


Fig. II.—Cubic close packing projected upon octahedral face (111), showing planes of symmetry. A cubic cell is outlined in center, being viewed looking down upon its solid angle which is in center of diagram. The dotted circles represent lower, the light circles intermediate, and heavy circles upper layer of spheres.

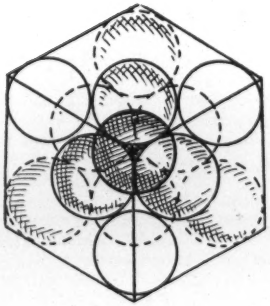


Fig. III.—Cubic cell, looking down upon solid angle.

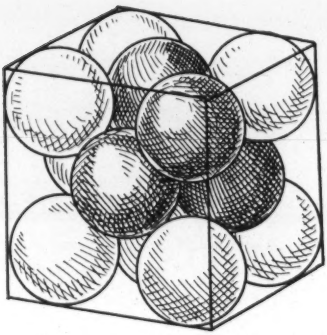


Fig. IV.—Cubic cell seen from side. Four spheres forming a tetrahedron are shaded more heavily.

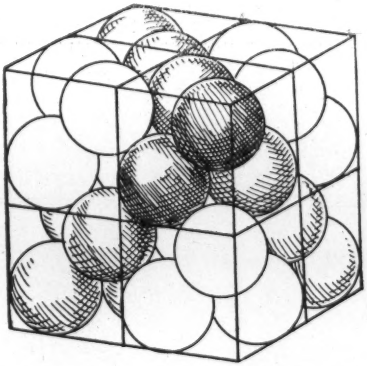


Fig. V.—Cubic cell seen from side. Small cells each occupied by four spheres which form tetrahedra.

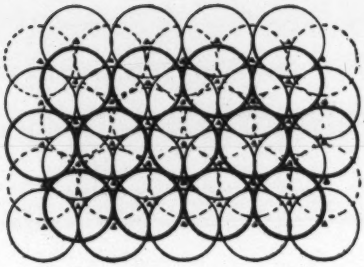


Fig. VI.—Projection of cubic close-packing seen upon the octahedral face (111). The dotted circles lie beneath, the light circles, are intermediate the heavy circles above.

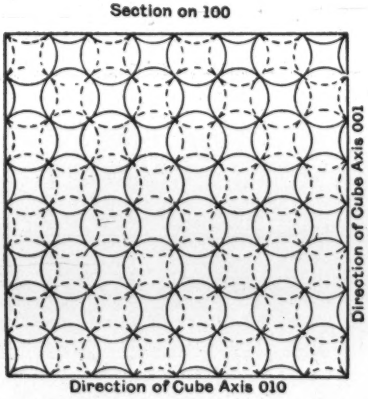


Fig. VII.—Cubic packing. Projection of spheres upon cube face (100).

c. Two-fold axes of symmetry pass through the centers of the spheres, normal to the rhombic dodecahedral face (Fig. VIII.).

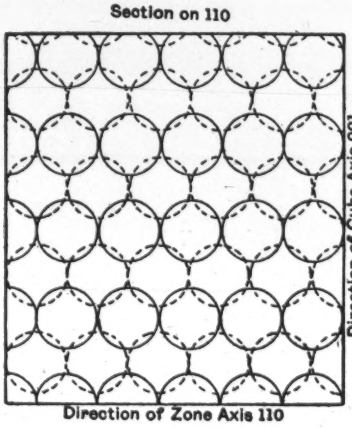


Fig. VIII.—Cubic packing. Projection of spheres upon face of the rhombic dodecahedron (110).

2. *Planes of Symmetry* pass through all the axes (Fig. II.).

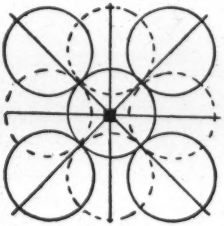


Fig. IX.—Symmetry of cubic packing seen on cube face (100).

The symmetry is well seen in the cubic cell, Fig. IV., as well as Fig. IX., where the four-fold symmetry of the cubic face is shown.

The resulting symmetry is that of the Normal (Holohedral) Group of the Isometric System, in which form, therefore, assemblages of this type should crystallize.

The spheres of atomic influence are viewed as deformable, though incompressible. In close packing so as to eliminate interstitial space, they become polyhedra, the number of whose faces equals the number of spheres with which they are in contact. In the cubic closest-packed assemblage each is in contact with twelve other spheres and hence becomes a rhombic dodecahedron, as seen in Fig. X.

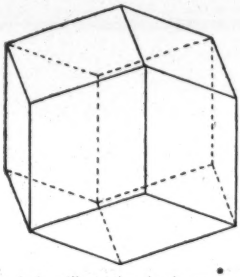


Fig. X.—Rhombic dodecahedron illustrating the shape assumed by the atomic sphere of influence in the cubic close packing.

Hexagonal Assemblage of Closest-packed Spheres.

Arrangement of Spheres.—In the hexagonal type of closest-packed spheres, illustrated in Fig. I., the third layer repeats the first. This assemblage may be viewed, for the purpose of visualizing it, as made of spheres which are close packed in hexagonal prisms. One of these prisms is outlined in Fig. XI., and shown separately in Fig. XII. and in perspective in Fig. XIII., where it is observed from the side marked *p*, *p'* in Fig. XII. It will be observed that certain of the spheres of the intermediate layer project beyond the limit of the cell and fit into corresponding cavities of adjoining cells.

This structure, like the preceding, may be viewed as made of tetrahedra, each of which consists of four spheres. The spheres of alternate tetrahedra are shaded in Fig. XI. A double layer of spheres may be considered as made of alternately inverted tetrahedra. In Fig. XI. the shaded tetrahedra have their apices directed upward, while the bases of the unshaded tetrahedra are directed upward.

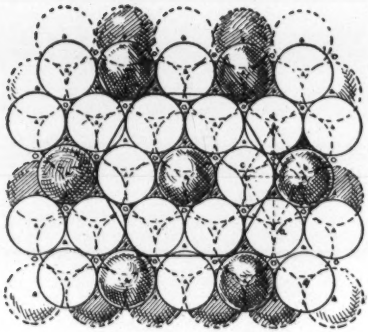


Fig. XI

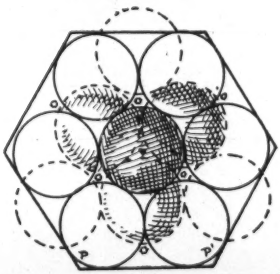


Fig. XII.—Projection of hexagonal cell upon basal pinacoid (0001).

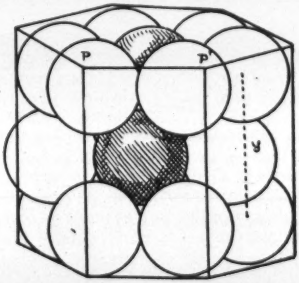


Fig. XIII.—Hexagonal cell seen in elevation. y = translation giving value of c axis.

Symmetry.—The hexagonal close-packed assemblage possesses the following elements of symmetry:

1. *Planes of Symmetry.*—Six sets of planes of symmetry occur normal to the basal pinacoid (0001), 3 sets being ordinary planes of symmetry (heavier lines, Fig. XIV.), and 3 sets are gliding planes of symmetry (lighter lines, Fig. XIV.). Added planes of symmetry pass parallel to the basal pinacoid, as seen in Fig. XIII.

2. *Axes of Symmetry.*—Six-fold screw axes lie in the openings between the spheres, at the intersection of the 6 planes of symmetry (Fig. XIV.). Three-fold axes of symmetry

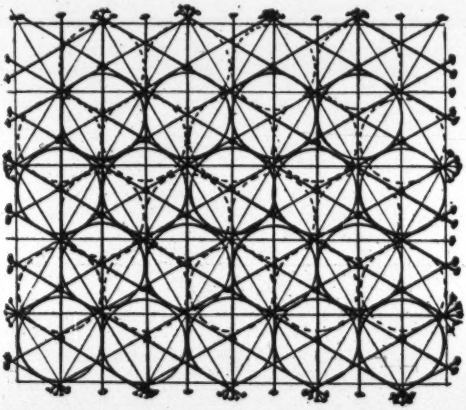


Fig. XIV.—Symmetry of hexagonal packing projected upon basal pinacoid (0001).

pass through the center of each sphere, being produced by the intersection of three planes of symmetry (Fig. XIV.). Horizontal two-fold axes of symmetry are formed at the intersection of the vertical and horizontal planes of symmetry (Fig. XIV.).

The resulting symmetry is that characteristic of the Normal (Holohedral) Group of the Hexagonal System in which group substances of this type should, therefore, crystallize.

Axial Ratio.—The axial ratio may be determined as follows: If the distances between like points in the structure are termed the translation distances (or more simply the translations),

then, according to the Raumgitter theory, the axial ratios are the ratios of the translations distances. It is therefore simply necessary to determine the translation distances. Thus, in Fig. XI., the horizontal translation a is cb which is equal to ab or ad, while the vertical translation c is y (Fig. XIII.). Their relative values are illustrated in Fig. XV.

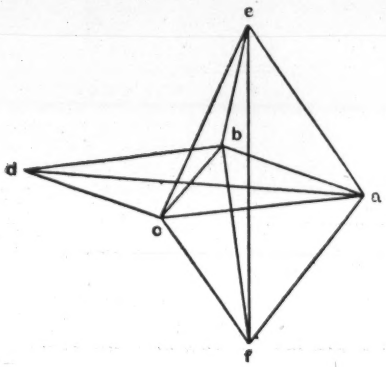


Fig. XV.—Axial ratios of hexagonal close-packed assemblage.

These quantities are easily determined as follows: Let the diameter of the spheres equal 1. Then in Fig. XI., abc is an equilateral triangle in which $bc = 1$ and $ad = \sqrt{3}$. y is twice the altitude of a tetrahedron whose side is 1 (see Figs. XI. and XIII.), hence, $y = 2\sqrt{\frac{2}{3}}$. Two alternative ratios may be used:

(1) The a axis may be chosen in the direction cb, whence $a = 1$ and $c = y = 2\sqrt{\frac{2}{3}} = 1.6330$, and

$$c : a = 1.6330 : 1.$$

One-half of the above ratio may be used, giving

$$c : a = 0.8165 : 1.$$

(2) The a axis may be chosen in the direction ad. The a and c directions intersect, as seen in Fig. XV., at one-third

the length of *ad*. We therefore use $a = \frac{1}{3}\ ad\ = \frac{1}{3}\sqrt{3}$, and $c = \frac{1}{2}\ y = \sqrt{\frac{2}{3}}$, whence

$$c : a = 1.4142 : 1.$$

Modifications of the Ideal Assemblages.

The ideal assemblages, above discussed, are produced by the closest packing of spheres of identical volumes. The actual assemblages are believed, in many cases, to depart from the ideal forms in that the spheres of influence of atoms of the same valence, though approximating equality, may not have absolutely the same volume. The actual assemblages, though approaching the ideal, may, therefore, differ from the ideal in possessing a lower grade of symmetry, and in manifesting a slight departure from the ideal axial ratios. It is believed by the authors, however, that equivalent atoms closely approximate equivalency of volume, so that the departures from the ideal forms should, in general, be slight.

If the views of the authors are correct, therefore, all assemblages of equivalent atoms should crystallize in the Isometric or Hexagonal Systems (or in slight modifications of forms belonging to these systems), and should possess axial ratios which closely approximate those of the ideal assemblages. By comparing the actual with the ideal forms, it should be possible to make a somewhat rigid test of the correctness of their theories. This they proceed to do, discussing first the crystal forms of the elementary bodies and secondly the forms produced by combinations of atoms of the same valence.

CRYSTAL FORMS OF THE ELEMENTS.

The spheres of influence of atoms of the same element would be expected to have the same volume. The elements appear, therefore, to be particularly well adapted to test the validity of the authors' conclusions.

The crystal forms of 40 elements are well known and are summarized in the following table.

Crystal Forms of the Elements.

		Per cent.
Crystallizing in the	Isometric System	50
" " "	Hexagonal "	35
" " "	Tetragonal "	5
" " "	Orthorhombic "	5
" " "	Monoclinic "	5
" " "	Triclinic "	0

An examination of the above table shows that 50 per cent of the elements crystallize in the Isometric System, though not all of them occur in the Holohedral Group of the ideal forms, some possessing a lower symmetry, *e. g.*, diamond, which is tetrahedral. The axial ratios of the isometric forms necessarily coincide with the ideal values.

Thirty-five per cent of the elements are hexagonal, most, though not all, being holohedral. The axial ratios approach the ideal values closely, although in most cases they are not absolutely identical with them.

Axial Ratios of Hexagonal Elements.

	Observed.	Ideal.
Glucinum	$a:c = 1:1.5802$	$= 1:1.6330$
Magnesium	$a:c = 1:1.6242$	$= 1:1.6330$
Zinc	$a:c = 1:1.3564$	$= 1:1.4142$
Cadmium	$a:c = 1:1.3350$	$= 1:1.4142$
Arsenic	$a:c = 1:1.4025$	$= 1:1.4142$
Antimony	$a:c = 1:1.3236$	$= 1:1.4142$
Bismuth	$a:c = 1:1.3035$	$= 1:1.4142$
Tellurium	$a:c = 1:1.3298$	$= 1:1.4142$

An examination of the above table shows that 85 per cent of the elements closely approach the ideal forms. Two reasons are suggested for the slight deviations of the observed from the ideal forms. First, imperfection of measurement. Arsenic and magnesium have been measured more carefully than any other of the hexagonal elements and are found to approach most closely to the ideal values. Not all the differences can be accounted for in this manner, however. The authors accordingly suggest that the slight deviations of the observed from the ideal axial ratios, as well as the lowering of the grade of symmetry, are due to slight differences in the volumes of the spheres of atomic influence of atoms of the same element. They show that a slight expansion of every fourth sphere will give the ratios observed in the hexagonal elements.

Iodine, tin, sulphur, and selenium crystallize in other systems, though all closely approach isometric or hexagonal forms. Iodine is orthorhombic with $a:b:c$ almost precisely $2:3:4$, an isometric ratio. Tin crystallizes both in the Tetragonal and Orthorhombic Systems. If one-half of the spheres were to become slightly smaller than the others in the ideal cubic assemblage, the forms observed would result. Sulphur possesses four crystal forms, one orthorhombic, two mono-

clinic, and one trigonal. It is shown that the dimensions observed would result if one-third of the spheres were somewhat smaller than the others, the different forms being due to slight differences of arrangement. The crystal form of selenium, which is monoclinic, is explained in a similar manner.

The application of the authors' theories to the crystal form of the elements offers the most direct test of the validity of their views. It is seen that there is a striking general conformity between prediction and observation, associated with certain persistent differences. While eighty-five per cent crystallize in the predicted systems, there is, in some cases, a lowering of the grade of symmetry from the holohedral to less symmetrical groups. The axial ratios are necessarily precise in the Isometric System, but in the Hexagonal System they manifest departures from the ideal values which, though slight, are, at least in a number of cases, too great to be explained as errors of observation. Certain of the elements depart still more widely from the predicted form. It becomes necessary, therefore, to admit that, if the authors' views are correct, the volumes of the spheres of atomic influence *of the same elements* vary within narrow limits. The authors believe this to be the case, attributing it to some form of preferential treatment of certain of the spheres. The cause of such preferential treatment in a homogeneous structure is, however, not apparent. It remains to be seen how acceptable their idea will prove in the future. With these qualifications, the conformity of the observations with the theory is impressive.

COMBINATIONS OF EQUIVALENT ATOMS.

If the volume is proportional to valence, it is manifest that combinations of atoms of the same valence should crystallize in the Hexagonal or Isometric Systems or exhibit some slight modification of these systems, and should possess axial ratios which closely approximate those of the ideal assemblages. Since there are large numbers of such bodies, it should be possible to submit the authors' views to an extended test. In order to do so they discuss first the binary compounds, and then compounds of more complex character.

1. *Binary Compounds.*

The following table shows the crystal forms of 67 binary compounds examined by the authors.

Crystal Forms of Binary Compounds.

	Per cent.
Crystallizing in the Isometric System	68.5
" " " Hexagonal "	19.5
" " " Tetragonal "	4.5
" " " Orthorhombic "	3.0
" " " Monoclinic "	4.5
" " " Triclinic "	0.0

From the above table it is seen that 88 per cent of the forms studied crystallize either in the Isometric or the Hexagonal Systems. Seven forms do not crystallize in the Isometric or Hexagonal Systems, *viz.*, Hg_2Cl_2, Hg_2I_2, FeAs, AsS, AgF, PbO, HgO, CuO. Of these, however, two are compounds of atoms not strictly of the same valence, while mercury and copper present certain anomalies of valency. The volume of the fluorine atom also will be shown to depart considerably from the normal volume of a univalent element. The conformity of the observed and predicted systems is, therefore, very close.

When we examine the crystal group of the bodies, we find that most do not crystallize in the Holohedral Groups of the ideal assemblages. This feature is believed by the authors to be due to slight inequalities in the volumes of the atoms of the different elements, and conforms to the third law.

The relation of the observed to the ideal axial ratio is illustrated by the following five compounds which crystallize in the Hexagonal System and which have been well studied.

Axial Ratios of Hexagonal Binary Compounds.

	Observed.	Ideal.
GlO	$a:c = 1:1.6305$	1:1.6330
ZnO	$a:c = 1:1.6077$	1:1.6330
ZnS	$a:c = 1:1.8175$	1:1.8165
CdS	$a:c = 1:1.8109$	1:1.8165
AgI	$a:c = 1:1.8196$	1:1.8165

An examination of the above axial ratios shows that they closely approach the ratios of the ideal compounds though they are not absolutely identical with them.

The authors make elaborate studies of silver iodide and the alkali halogen compounds to see how far both their dimensions and their physical properties may be explained by the assumptions made.

Silver Iodide.

This salt is dimorphous, crystallizing in the Isometric and Hexagonal Systems. The isometric form appears to be holohedral, the hexagonal form is hemimorphic. The axial ratio of the hexagonal modification is $a:c = 1:8196$ (the ideal value = 1:8165).

Structure.—It was shown in a preceding paragraph that the isometric assemblage may be regarded as made of tetrahedra possessing like orientation, as illustrated in Fig. V. If alternate tetrahedra are replaced by silver spheres while the remaining tetrahedra consist of iodine spheres, an assemblage is produced which represents the cubic modification of silver iodide, according to the views of the authors. This is illustrated in Fig. V., the shaded tetrahedra representing the silver spheres and the unshaded the iodine spheres. In a similar manner they may be combined to produce the hexagonal modification illustrated in Fig. XI.

Symmetry.—The isometric assemblage possesses the holohedral symmetry observed in crystals of silver iodide. In the hexagonal structure, shown in Fig. XI., the tetrahedra of one kind have their apices directed upwards (the shaded tetrahedra) while those of the other kind have their bases directed upwards. This structure possesses vertical but no horizontal planes of symmetry and should therefore be hemimorphic. The observed crystals of the hexagonal modification of silver iodide are hemimorphic. The very slight departure from the ideal axial ratio would be explained by a very slight difference in the volumes of the silver and iodine spheres. The crystal forms may hence be predicted from the structure.

Physical Properties.—The crystals of silver iodide possess unusual properties. The hexagonal variety exhibits a negative coefficient of expansion parallel to the *c* axis and a small positive coefficient in directions at right angles to it. Upon heating to 145°–147° it undergoes a transformation into the cubic modification with explosive energy and maintains this form at higher temperatures.

These properties may be explained as follows. It has been shown that silver expands more rapidly than iodine for equal increments of temperature. If this property is manifested by the atoms, and the silver atoms are very slightly smaller than the iodine atoms at low temperatures, then, with increasing temperature they would approach equality of volume. As they approach this condition the structure will become more close-packed, *i. e.*, it will manifest the negative coefficient

of expansion observed in the *c* direction. It would, however, expand slightly in a direction normal to it, since the atoms are in contact in that plane, as seen in Fig. I. When the atoms become equal in volume a slight shear would suffice to transform the whole assemblage to the cubic modification. Upon further heating it would manifest a positive coefficient of expansion, since the structure is becoming less ideally close-packed. If the volumes of the iodine and silver atoms become equal at 145°–147° we can understand the transformation at that temperature. Both the crystal form and physical properties of silver iodide would therefore result from the structure given.

ALKALI HALIDES.

The authors discuss at some length the various members of the group comprising the chlorides, bromides, and iodides of potassium, caesium, and sodium and related elements, all of which crystallize in the Isometric System and probably in the gyrohedral division of Groth (plagihedral, Dana) which is characterized by possessing many axes but no planes of symmetry.

Structure.—It is suggested that the structure is fundamentally the same as in silver iodide, the metals replacing tetrahedra alternating with those formed by the halogen atoms, as in Fig. V. If the atoms of the metal differ slightly in volume from those of the halogen, the differences being greater than in the case of silver and iodine, the resultant structure would not be close-packed. In order to produce close packing a slight distortion of the tetrahedra is necessary whereby they are transformed into triangular pyramids which slip slightly upon each other in the final adjustment. The result is a structure which is shown to have no planes of symmetry, but which retains its axes of symmetry. In other words, the structure possesses the symmetry of the Gyrohedral Group of the Isometric System in which these salts are observed to crystallize.

Physical Properties.—Most of the crystals of this family possess the following properties: (1) octahedral twinning; (2) elongation in the direction of the three-fold or four-fold axis of symmetry when the salts crystallize from impure solutions; (3) cubic cleavage; (4) gliding in the rhombic dodecahedral face, the translation direction being parallel either to the shorter or longer diagonal of the face. The explanation of these numerous properties presents a difficult test of the theory proposed. All are shown to spring, however, from the fundamental assumptions contained in the theory.

Since the three-fold axes of the crystal are differently terminated at their two extremities, as shown in Fig. V., it is possible to select a given plane of spheres normal to the axes and to build up the structure in a precisely similar manner in two directions from the plane. In this manner the plane becomes a plane of symmetry, *i. e.*, a twin results, the twinning plane being the octahedral face.

Elongation is shown to arise by methods of twinning about the three-fold or four-fold axis in which no new faces are developed, while the phenomena of gliding and cleavage are likewise shown to result from the structures assigned. Thus both crystal form and crystallographic properties are explained by the principles employed.

MORE COMPLEX BODIES.

Among the most interesting bodies discussed are the trihalogen derivatives of the type of CsI_3, of which a large number are considered. All of these are orthorhombic save KCl_2I, which is monoclinic, and $CsCl_2I$, which is dimorphous. The structure assigned is built of layers one of which is illustrated in Fig. XVI., the heavy circles representing the metallic base. They are superposed in the hexagonal close packing, as shown

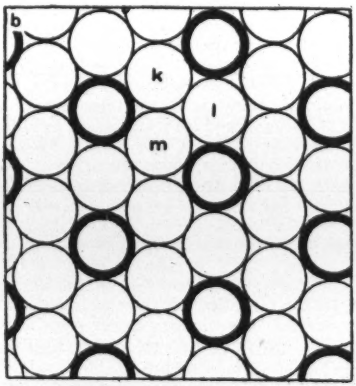


Fig. XVI.—Projection of a single layer of spheres of CsI_3. The heavy circles represent the Cs spheres.

in Fig. XVII. The symmetry would be trigonal were the atoms of equal volume. It becomes orthorhombic, as observed in the crystals, if the atoms of the different elements differ in volume, while it is shown that slight modifications may give rise to the two exceptional forms. If the axial ratio is written upon three axes then, in the ideal case in which the atomic spheres have equal volumes, $a : b : c = 0.6124 : 1 : 1.0608$, whence the ideal equivalence parameters[1] are $x : y : z = 1.1224 : 1.8329 : 1.9443$.

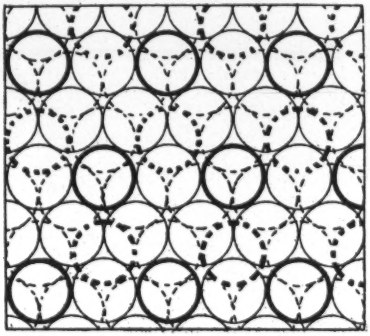


Fig. XVII.—Projection of CsI_3 upon the basal pinacoid (0001) in hexagonal close packing.

In most of the bodies, the observed ratios differ from those of the ideal assemblage. These differences lead to important deductions concerning the relative volumes of the spheres of influence of different elements.

The Principle Involved.—In Fig. XVII. the spheres are in contact in the horizontal line. If now the darker spheres (representing the metal) increase in size, the structure expands horizontally; in other words, the value of x increases, *i. e.*, *x is a minimum in the ideal case.* As the volumes of the metallic spheres increase the structure will contract in a direction normal to x, since the hollows between adjacent lines of spheres become deeper, permitting them to approach nearer together. *Hence y is a maximum in the ideal values.* In other words,

[1] See abstract of preceding paper of Barlow and Pope (THIS JOURNAL, **38**, 642) for a discussion of equivalence parameters.

an increase in the volume of the spheres of atomic influence of the base, as compared to those of the halogen, will result in a difference between the observed and the ideal values, whereby x increases and y diminishes, the amount of the deviation indicating the relative difference in the volumes of the constituent spheres of atomic influence. The following table shows such differences and permits a calculation of the differences of volume which would account for the deviations observed.

	x.	y.	z.
$RbCl_2Br$	1.2135	1.6982	1.9410
$CsCl_2Br$	1.2250	1.7047	1.9155
$RbBr_2Cl$	1.2060	1.7180	1.9360
$RbCl_2I$	1.2169	1.6576	1.9830
$CsCl_2I$	1.2219	1.6572	1.9754
RbClBrI	1.2166	1.6733	1.9651
CsClBrI	1.2114	1.6756	1.9705
$RbBr_3$	1.2017	1.7286	1.9255
$CsBr_3$	1.2132	1.7652	1.8678
KBr_2I	1.2058	1.6845	1.9694
$RbBr_2I$	1.2044	1.6892	1.9662
$CsBr_2I$	1.2116	1.6821	1.9826
$CsBrI_2$	1.1877	1.7173	1.9610
RbI_3	1.1875	1.7316	1.9452
CsI_3	1.1901	1.7440	1.9273
KI_3	1.1846	1.7350	1.9461
Ideal	1.1224	1.8329	1.9443

An examination of the preceding table shows that x is always larger and that y is always smaller in the observed than in the ideal case, in agreement with the above deduction. This indicates that the spheres of influence of the metallic atoms are larger than those of the halogens combined with them. Again, the differences produced by the substitutions of the halogens are less than those produced by the substitution of the metals, indicating that the halogens differ less among themselves than they do from the metals. A comparison of the results produced by the substitution of the halogens in compounds of the same metal, as illustrated by the case of the rubidium salts, shows that the iodine sphere of influence is the largest, that of bromine is intermediate, while that of chlorine is smaller. An examination of the fluorine compounds shows that the sphere of influence of the flourine atom is still smaller. These results harmonize with the position of these elements in the Periodic System. In a similar manner it is shown

that, of the three bases, potassium, rubidium, and caesium, the sphere of influence of potassium is smallest, that of rubidium intermediate, and that of caesium largest.

These observations lead to the *fundamental conclusion that the volumes of the spheres of influence of the atoms of different elements of the same valency are approximately equal, while they may differ by slight amounts in harmony with their relations in the Periodic System.*

In addition to those discussed in the foregoing outline, many other compounds of equivalent elements are examined. While the results are not so conclusive in all cases, they nevertheless harmonize well with the fundamental conceptions of the authors.

The communication summarized in the above abstract is a notable contribution to the theories concerning the relation between crystalline form and chemical constitution, and is a fundamental addition to the previous discussion of the authors. The wealth of the data reviewed, the far-reaching deductions drawn, and the simplicity of the principles advanced render it worthy of high esteem. The general harmony of theory and observation is very suggestive, while the large number of crystallographic facts for which an explanation is here offered is impressive. There are, on the other hand, certain elements of artificiality in the methods of arriving at the resultant structures which need to be overcome. Further investigation of the differences in the volumes of the atoms of the equivalent elements may remove this difficulty. In the meanwhile, a working hypothesis of much value is offered for the further investigation of the problem of the relation of crystalline form and chemical composition.

CHARLES K. SWARTZ.

REVIEWS.

EXERCISES IN PRACTICAL PHYSIOLOGICAL CHEMISTRY. By SIDNEY W. COLE, M.A. Cambridge: W. Heffer and Sons; London: Simkin, Marshall and Co. Price, 5 shillings.

In writing this little book the author has evidently been actuated by a desire to place before medical students a group of experiments which will yield the greatest amount of information for the least expenditure of time, and described in such a manner that a failure to bring about the desired conclusion shall be attributable only to carelessness or accident. The ground covered and the arrangement are so nearly coincident with those of the conventional laboratory manual that

no outline is required here. However, its simplicity, clearness, accuracy, and freedom from vagaries are so pronounced as to give the book a peculiar value for its evident purpose.

A final chapter on the "Detection of Substances of Physiological Interest" might with profit have been altogether abandoned or replaced by a short treatment of some one of the more important subjects (such as applications of the polarimeter, nucleic acids) which have been omitted in the interest of brevity. The last chapter is in such contrast to the remainder of this excellent book as to suggest the expression "examinations in medicine" used by the author in his preface.

WALTER JONES.

UNTERSUCHUNG UND NACHWEIS ORGANISCHER FARBSTOFFE AUF SPEKTROSKOPISCHEM WEGE. Von JAROSLAV FORMÁNEK, Tit. Professor in der k. k. böhmischen technischen Hochschule, Inspektor an der k. k. allgemeinen Lebensmitteluntersuchungsanstalt der böhmischen Universitäte. Unter Mitwirkung von DR. EUGEN GRANDMOUGIN, Professor im eidgenossischen Polytechnikum in Zürich. Zweite, vollständig umgearbeitete und vermehrte Auflage. Erster Teil. Mit 19 Textfiguren und 2 lithogr. Tafeln. Berlin: Verlag von Julius Springer. 1909. pp. viii + 257. Price, M. 12.

The book entitled "Spektralanalytischer Nachweis künstlicher organischer Farbstoffe," which was published by Professor Formánek in 1900, marked the first attempt to introduce spectral analysis as a general method in the study of dyestuffs. Since then, this method has gained many adherents. Of the importance of the spectroscope in this field of chemistry, there is no longer any doubt. In a private communication to the author, Dr. Robert E. Schmidt, Director of the Farbenfabriken vorm. Fr. Bayer und Co., says: "In fact, I introduced the spectroscope into my laboratory almost twenty years ago and it has been of the greatest help to us in our work. Many discoveries would never have been made without this little instrument, and the manufacture of many products would be impossible without its aid." In the present book, after a general discussion of the spectroscopic method, absorption spectra of colored solutions, the influence of various factors, such as solvents, concentration, temperature, reagents, etc., on the spectra, Professor Formánek takes up the relations between color absorption, fluorescence and the constitution of colored bodies in general. He then discusses the relations between the constitution and absorption spectra of the following classes of dyes: di- and triphenylmethane dyes, fluorindene and triphendioxazin, acridin dyes, and anthraquinone dyes. In Part II., which is to appear soon, will be described the spectroscopic method of analysis of the most

important commercial dyestuffs and mixtures of them, together with their absorption spectra. C. A. R.

ION. A Journal of Electronics, Atomistics, Ionology, Radioactivity, and Raumchemistry. Edited by FREDERICK SODDY and CHARLES H. WALTER, in consultation with SV. ARRHENIUS, W. H. BRAGG, A. S. EVE, O. HAHN, W. H. JULIUS, A. WERNER, G. BRUNI, MD. CURIE, GUILLEAUME, VAN'T HOFF, W. MARCKWALD, M. WIEN.

This will be recognized as another new journal, and of the making of scientific journals, as of the making of books, there seems to be no end. The scope of this journal is indicated by the title and sub-title. The latter cannot be regarded as ideal English, and is not consistent. "Raumchemistry" would hardly pass in any country which used the English language, especially since the word admits of such easy translation. The inconsistency of "Electronics, atomistics, ionology," is obvious. Give us either "Electronics, atomistics, ionistics," or perhaps the less euphonius "Electronology, atomology, ionology." The reason for starting this journal, together with its aim, is stated thus by Mr. Walter. After calling attention to the richness of German scientific literature, and the influence of the German journals on the development of the special branches of science in that country, Walter says that "although physico-chemistry is an established department of science, it has no particular organ to represent it in England; and English authors had to rely upon the papers and magazines of various societies, whose columns were open to numerous other studies as well. Ion will be, therefore, the Physico-Chemical Journal of Britain."

Here again the tendency to manufacture words manifests itself. The term physical chemistry has pretty well established itself, and is not likely to give place for some time to physico-chemistry, or to anything else; and why should it, since the former is certainly more euphonius than the latter.

The contents of this number are inviting. A brief sketch of Becquerel is followed by a paper by Soddy on "The Charge Carried by the α-Particle." There is also a very interesting paper by Joly on "Uranium and Geology," and a contribution by Julius on the "Transmission of Energy in the World of Electrons."

Hahn and Meitner also have a paper on "Actinium C, A New Quickly Decaying Product of Actinium."

The number contains also several "reports" on matters of interest, especially in the field of radioactivity. May this journal meet with all the success that it deserves. H. C. J.

ELEKTROLYTISCHE ZÄHLER. Von DR. KONRAD NORDEN. Halle a/S: Verlag von Wilhelm Knapp. 166 pp., 130 illustrations. 1908. Price, M. 9.

The thirty-third of a series of monographs on applied chemistry. In view of the present narrow use of the electrolytic meter in the sale of electric power the purpose of the work is the investigation of the limits imposed on the meter by its principles, and of the degree in which the requirements of practice may be met.

In Part I the qualities demanded of the practical electric meter are first treated. The conditions and limits of accuracy, overload, no load, power loss, variation of voltage, are considered at length. The suitability of the electrolytic cell as based on Faraday's laws for meeting all these conditions then follows. The principal objections to the use of the electrolytic meter are unsuitability to three-wire service and two-rate service and entire exclusion from alternating current service.

In Part II the electrolysis of the salts of copper, zinc, silver, mercury, and the electrolysis of water are treated with special consideration of inherent peculiarities as affecting the permanency and constancy of a meter. A valuable feature of this part are the lists of references covering the literature on each type of electrolytic cell. A discussion of the work of the investigator is frequently given.

Part III contains extensive descriptions of the most important types of electrolytic meter which have appeared, with frequent references to patents and literature. The difficulties met in practice with each type are discussed. Some fifty or sixty types involving solid, liquid and gaseous decomposition products are described.

Since the accepted standard of current is defined in terms of the electrolytic deposition of silver, and since the most convenient and accurate laboratory methods for the measurement of current are those of electrolysis, it would appear that the principles involved in these methods would find valuable application in commerical measuring instruments. Many early attempts, notably those of Edison, were made to produce such instruments but the necessary conditions of accuracy and reliability are not met in the circumstances under which such meters are used. Electrolytic meters are practically unknown in this country, and constitute, according to Dr. Norden, less than 5 per cent of the total number of meters abroad. The work is valuable in that it collects for the first time the results of experience with this type of apparatus.

J. B. WHITEHEAD.